

DISTRIBUTION OF ISOMORPHIC AND ISODIMORPHIC COMPONENTS BETWEEN THE
SOLID AND LIQUID PHASES DURING CRYSTALLIZATION FROM AQUEOUS SOLUTIONS

III. EQUILIBRIUM IN THE SYSTEM $\text{Co}(\text{NO}_3)_2 - \text{Ni}(\text{NO}_3)_2 - \text{H}_2\text{O}$ AT 20° [1]

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According to the literature data, cobalt nitrate and nickel nitrate crystallize in the form of hexahydrates which have identical structures and close crystal lattice parameters [3].

The solubility of these salts is also almost identical. In view of the closeness of the properties of both salts it could be assumed that they are isomorphous and form solid solutions at all possible component ratios. However, as will be evident from the following, cobalt nitrate and nickel nitrate are actually isodimorphic at 20° and have differing crystalline structures. The elucidation of these structures must be the subject of a special study.

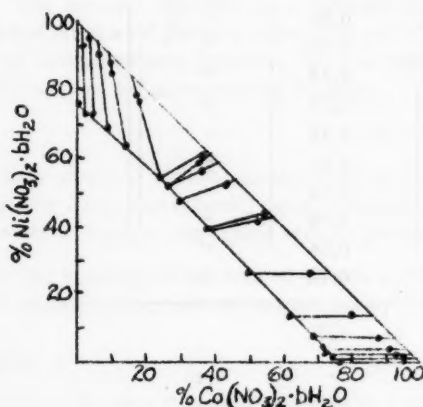


Fig. 1. Equilibrium composition diagram for the system $\text{Ni}(\text{NO}_3)_2 - \text{Co}(\text{NO}_3)_2 - \text{H}_2\text{O}$ at 20° .

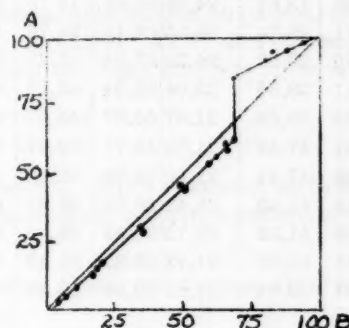


Fig. 2. Phase distribution diagram for the system $\text{Ni}(\text{NO}_3)_2 - \text{Co}(\text{NO}_3)_2 - \text{H}_2\text{O}$ at 20° .
A) % $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the solid phase,
B) % $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the salt component of the mother liquor.

The methods of analysis were analogous to those indicated in the description of the results of the investigations of the system: $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 - \text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ [2].

The experimental results are given in the table, in the equilibrium composition diagram (Fig. 1) and in the diagram of the phase distribution of components (Fig. 2).

As is evident from the curves, two series of solid solutions are formed in the system at 20° : one series with a crystal structure of the cobalt nitrate type, and the other of the nickel nitrate type. Cobalt nitrate and nickel nitrate are thus isodimorphic at 20° . In the last two columns of the table the magnitudes of the equilibrium distribution coefficients of the components for various points of each of the two series of solid solutions are given. The magnitude of the equilibrium distribution coefficient of nickel salt in relation to cobalt salt $D_{(\text{Ni}, \text{Co})}$ is identical in value over the entire region in which solid solutions of the cobalt nitrate type exist, and on the average is equal to 0.72; a single value for the equilibrium distribution coefficient of cobalt salt relative to nickel salt $D_{(\text{Co}, \text{Ni})}$ is also obtained for the region in which solid solutions with a nickel nitrate structure exist, and is equal on the average to 0.42.

TABLE

Equilibrium in the System $\text{Co}(\text{NO}_3)_2 - \text{Ni}(\text{NO}_3)_2 - \text{H}_2\text{O}$ at 20° . [I] % $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; II] % $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; III] % H_2O

Expt. No.	Analytical results						Composition of the solid phase		Distribution coefficient		Notes	
	for the mother liquor			for the solid phase			the solid phase		D _{eq.} (Ni, Co)	D _{eq.} (Co, Ni)		
	I	II	III	I	II	III	I	II				
1a	77.07	—	22.93	—	—	—	—	—	—	—	Solid solutions with a cobalt nitrate structure	
3a	75.17	0.88	23.95	94.26	0.83	4.91	99.19	0.81	0.69	—		
19a	75.55	0.90	23.55	95.79	0.79	3.42	99.22	0.78	0.71	—		
19b	75.42	0.85	23.73	96.33	0.80	2.87	99.21	0.79	0.71	—		
2a	72.82	2.66	24.52	93.22	2.53	4.25	97.52	2.48	0.68	—		
2b	73.60	2.67	23.73	92.60	2.63	4.77	97.38	2.62	0.72	—		
1a	73.23	3.84	22.93	91.35	4.06	4.59	95.92	4.08	0.82	—		
1b	72.64	4.10	23.26	91.63	3.98	4.39	96.05	3.95	0.73	—		
4a	68.94	8.03	23.03	88.05	7.70	4.25	92.37	7.63	0.71	—		
4b	69.25	8.02	22.73	88.92	7.82	3.26	92.21	7.79	0.78	—		
6a	69.75	8.03	22.22	88.74	7.71	3.55	92.35	7.65	0.72	—		
6b	69.40	8.02	22.58	88.06	7.86	4.08	92.17	7.83	0.73	—		
16a	62.02	13.70	24.28	79.67	13.83	6.50	86.13	13.87	0.73	—		
16b	61.95	13.67	24.38	80.81	14.15	5.04	85.72	14.28	0.75	—		
14a	49.71	26.74	23.55	68.46	26.76	4.78	73.24	26.76	0.68	—		
14b	49.80	25.97	24.23	67.54	27.23	5.23	72.40	27.60	0.73	—		
11a	38.11	38.85	23.04	53.34	42.23	4.43	56.97	43.03	0.74	—		
11b	38.84	39.59	21.57	55.37	43.67	0.96	56.15	43.85	0.77	—		
12a	30.81	47.49	21.70	43.71	52.97	3.32	46.05	53.95	0.76	—		
12b	30.88	47.54	21.58	43.94	52.86	3.20	46.22	53.78	0.75	—		
13a	26.15	51.43	22.42	36.53	56.61	6.86	41.10	58.90	0.73	—		
13b	25.98	51.29	22.73	35.39	58.25	6.36	39.08	60.92	0.79	—		
18a	24.44	53.83	21.73	36.22	61.12	2.66	38.02	61.98	0.74	—		
18b	24.34	53.84	21.82	35.68	60.43	3.89	38.25	61.75	0.73	—		
Average value of D:									0.72			
10a	24.70	54.32	20.98	17.37	78.14	4.49	15.38	84.62	—	0.40	Solid solutions with a nickel nitrate structure	
10b	25.16	53.45	21.39	17.89	77.38	4.73	15.83	84.17	—	0.40		
9a	14.84	63.49	21.67	9.91	87.73	2.36	9.31	90.69	—	0.44		
15a	14.53	63.11	22.36	9.99	84.70	5.31	8.51	91.49	—	0.40		
15b	14.51	62.47	23.02	10.03	86.81	3.16	9.26	90.74	—	0.44		
8a	8.82	69.02	22.16	5.63	90.94	3.43	5.02	94.98	—	0.41		
8b	8.78	69.01	22.21	5.57	90.74	3.69	4.93	95.07	—	0.41		
7a	4.71	73.84	21.45	2.96	95.06	1.98	2.79	97.21	—	0.45		
7b	4.76	73.80	21.44	3.03	94.38	2.59	2.79	97.21	—	0.44		
17a	2.08	73.30	24.62	1.39	93.36	3.25	1.20	98.80	—	0.44		
17b	2.09	72.74	25.17	1.47	92.74	5.79	1.28	98.72	—	0.45		
Average value of D:									0.42			
18a	—	76.21	23.79	—	—	—						

SUMMARY

The equilibrium in the system $\text{Co}(\text{NO}_3)_2 - \text{Ni}(\text{NO}_3)_2 - \text{H}_2\text{O}$ at 20° was studied. It was found that at this temperature the components are isodimorphic, and that two series of solid solutions are formed in the system. It was established that the systems are ideal in each of the two regions of existence of a solid solution with a definite structure.

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* See Consultants Bureau Translation, page 1355.

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THE HYDROGEN BOND AND THE VISCOSITY OF SOLUTIONS

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The formation of complexes due to hydrogen bonds between alcohol, phenol and acid molecules causes a sharp increase in the viscosity of liquids [1]. Inasmuch as the indicated complexes of molecules of dissolved substances survive in such solvents as benzene, an anomalously increased viscosity of benzene solutions of the substances under consideration is to be expected. Since the viscosity of liquids is determined not only by the coupling forces between molecules (including the hydrogen bond), but also by the mass of the molecules and the number of them in a unit volume, to detect the influence of the coupling forces it is reasonable to compare the values of the viscosity of solutions of identical-by-weight samples of the substances in a given volume of solution. In such solutions the increase in the mass of the molecules of the dissolved substance is accompanied by decrease in the number of molecules in a unit volume, and the difference in viscosity evoked by differences in the mass of the molecules is compensated for to a considerable extent by the differences in the number of molecules of the dissolved substance in a unit volume.

The results of viscosity measurements of the indicated type of solutions of 22 compounds (phenol, its derivatives and substituted phenols) in benzene at 50° are set forth in Table 1. As follows from the data obtained in the case of monosubstituted benzenes, the functional groups arrange themselves in a series according to the value of the viscosity of the corresponding solutions:



i.e., form solutions with the greater viscosity, the greater their group moment. Only a solution of the hydroxyl-containing compound (phenol) has an anomalously high viscosity and the OH group occupies a position in the series which does not correspond with its group moment.

The viscosity of solutions of phenol, cresols, m- and p-nitrophenols is greater than the viscosity of solutions of the corresponding methoxy compounds by $7-28 \cdot 10^{-5}$ poise.

TABLE 1

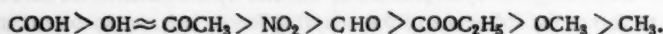
Viscosity of Benzene Solutions (Samples of 0.9984 - 0.9990 g in Approximately 25 ml of Solution) at 50° ± 0.1

Compound	$\eta \cdot 10^5$ poise	Difference in the viscosity of solutions		
		$\eta_{\text{m}} - \eta_{\text{o-}}$	$\eta_{\text{p-}} - \eta_{\text{o-}}$	$\eta_{\text{OCH}_3} - \eta_{\text{OH}}$
Nitrobenzene	443			
Nitrophenol: o-	443			
m-	455	+12		
p-	458		+15	
Nitroanisole: o-	454			+11
m-	448	-6		-7
p-	449		-5	-9
Acetophenone	442			
Hydroxyacetophenone: o-	453			
p-	482		+29	
Methoxyacetophenone: o-	456			+3
m-	454	-2		
p-	454		-2	-28
Toluene	436			
Cresol: o-	462			
m-	458	-4		
p-	464		+2	
Cresyl methyl ether: o-	447			-15
m-	444	-3		-14
p-	445		-2	-19
Phenol	449			-
Anisole	440			-9

Compounds with a hydrogen bond within the molecule (o-nitrophenol and o-hydroxyacetophenone) differ from the m- and p-isomers which are associated intermolecularly in solution. Thus, their methyl ethers yield solutions with a viscosity not lower but higher than that of solutions of the initial hydroxy compounds. While solutions of o-, m- and p-isomers ordinarily have almost the same viscosity, solutions of o-isomers with intramolecular hydrogen bonds within them have an appreciably smaller viscosity (of the order of $15-29 \cdot 10^{-5}$ poise) than their m- and p-isomers.

It is characteristic that all the relationships noted for benzene solutions are observed in the case of alcoholic solutions of the indicated substances.

In Table 2 are set forth the results of viscosity measurements of alcoholic solutions of 37 compounds of the indicated type (phenol, benzoic acid and their substituted and derived compounds). The functional groups (except OH and COOH) also arrange themselves by value of the viscosity of solutions of monosubstituted benzenes in alcohol in a series which basically agrees in order with that of their group moment:



In alcohol phenol, and particularly benzoic acid also yield solutions with an anomalously high viscosity related to the influence of intermolecular association. The viscosity of a solution of m- and p-hydroxyacetophenones is greater than the viscosity of a solution of the metamer m- and p-methoxybenzaldehydes by 3-5%. Alcoholic solutions of methoxy compounds, like benzene solutions, have an appreciably smaller viscosity than their initial hydroxy compounds. Solutions of esters of the acids (benzoic and hydroxybenzoic) also have a sharply reduced viscosity in comparison with that of solutions of the acids themselves.

TABLE 2

Viscosity of Alcoholic Solutions (Samples of 0.9984-0.9990 g in Approximately 25 ml of Solution) at $50^\circ \pm 0.1$

Compound	$\eta \cdot 10^5$ poise	Difference in the viscosity of solutions			
		$\eta_{\text{m}} - \eta_{\text{o}}$	$\eta_{\text{p}} - \eta_{\text{o}}$	$\eta_{\text{OCH}_3} - \eta_{\text{OH}}$	$\eta_{\text{COOC}_2\text{H}_5} - \eta_{\text{COOH}}$
Nitrobenzene	721				
Nitrophenol: o-	698				
m-	724	+ 26			
p-	728		+ 30		
Nitroanisoie: o-	717			+ 19	
m-	716	- 1		- 8	
p-	722		+ 5	- 6	
Acetophenone	726				
Hydroxyacetophenone: o-	725				
m-	760	+ 35			
p-	775		+ 50		
Methoxyacetophenone: o-	726			+ 1	
m-	731	+ 5		- 29	
p-	733		+ 7	- 42	
Benzaldehyde	718				
Hydroxybenzaldehyde: o-	729				
m-	765	+ 36			
Methoxybenzaldehyde: o-	733			+ 4	
m-	737	+ 4		- 28	
p-	737	+ 4			
Ethyl hydroxybenzoate: o-	708		+ 4		- 28
m-	751	+ 43			- 46
p-	751		+ 43		- 63
Toluene	682				
Cresol: o-	738				
m-	741	+ 3			
p-	743		+ 5		
Cresyl methyl ethers: o-	704			- 34	
m-	701	- 3		- 40	
p-	702		- 1	- 41	
Phenol	726				
Anisole	693			- 33	
Benzoic acid	734				
Hydroxybenzoic acid: o-	736				
m-	797	+ 61			
p-	814		+ 78		
Ethyl benzoate	711				- 23

Compounds with an intramolecular hydrogen bond, in contrast to their intermolecularly associated m- and p-isomers, yield solutions with a viscosity even lower than that of their methyl ethers and their non-associated meta-mers (o-hydroxyacetophenone and o-methoxybenzaldehyde) in spite of the presence of the hydroxyl group. In alcohol o-hydroxyacetophenone, o-nitrophenol, o-hydroxybenzoic acid, o-hydroxybenzaldehyde and ethyl o-hydroxybenzoate also tend to form an intramolecular hydrogen bond and to yield solutions which have an appreciably lower viscosity than that of their m- and p-isomers. All these correlations between the properties of the isomers are absent in the cresols, the o-isomer of which does not form an intramolecular hydrogen bond.

Thus, the same relations for the viscosities of alcohol solutions of non-associated and associated inter- and intramolecular compounds are found as for benzene solutions. Judging by certain data [2], such a relation also exists for the viscosity of 0.01 N solutions in amyl acetate; evidently in alcoholic solutions of the concentration under consideration the tendency of molecules of the dissolved substance, at least in part, toward the formation both of intramolecular hydrogen bonds and toward the formation of complexes between molecules due to the hydrogen bond is maintained. Data for the density of solutions [3] also leads to similar conclusions.

The correlations for the viscosity of solutions established above are identical with those detected for the viscosity of individual substances in the liquid state. This permits an estimate to be made from the data for the viscosity of solutions of corresponding compounds concerning the presence and character of association of a dissolved substance; this is particularly important for compounds which decompose on fusion.

EXPERIMENTAL

The synthesis and purification of the substances which were studied was carried out in accordance with the literature data. The purification of the solvents was described in the preceding article [3]. The relative viscosity was measured in an Ostwald viscosimeter. The viscosimeter was calibrated with the corresponding pure solvent. The measurement was carried out in a viscosimeter with the time of outflow for benzene equal to 279.9 seconds; for cresol solutions a viscosimeter was used with a time of outflow for benzene of 67.2 seconds. In the determination of the viscosity of alcoholic solutions the time of outflow of pure alcohol amounted to 120.0 and 129.2 seconds. In the calculations $\eta \cdot 10^5$ at 50° and the density were taken as 436 and 0.8464 for benzene, and as 702 and 0.7778 for alcohol. The value of the density of the solutions, necessary for the calculation of the value of η [3] was simultaneously determined. The data set forth in the tables for the viscosity of the solutions are the averages of several experiments which deviated from each other by not more than 0.4%.

SUMMARY

1. The values for the viscosity of solutions at 50° in benzene and in ethyl alcohol were determined for a number of phenols and acids and their esters.
2. It was established that the same relationships of the viscosities of non-associated and associated inter- and intramolecular compounds apply to benzene and alcohol solutions as to the individual substances in the liquid state.
3. The data for the viscosity of solutions of corresponding compounds can be utilized for the qualitative determination of the presence and character of association of a dissolved substance.

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* See Consultants Bureau Translation, page 73.

THE REACTION OF NITRATES OF METALS OF THE FIRST GROUP OF THE D. I. MENDELEEV PERIODIC TABLE WITH CADMIUM NITRATE IN MELTS

I. CONDUCTANCE OF THE BINARY SYSTEMS: LITHIUM NITRATE-CADMIUM NITRATE AND SODIUM NITRATE-CADMIUM NITRATE IN MELTS

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The chemistry of nitrates in melts has been relatively little investigated. At the same time the study of the character of the reaction of nitrates in the fused state is of practical and theoretical interest.

Experimental material on the specific conductance and numerical values of the absolute and relative temperature coefficients for the two binary systems: $\text{LiNO}_3\text{-Cd(NO}_3)_2$ and $\text{NaNO}_3\text{-Cd(NO}_3)_2$, the phase equilibrium diagrams of which, obtained by a visual-polytherm method of physico-chemical analysis, have already been described [1, 2], is presented in the present communication.

According to the literature data known to us, a total of only four binary nitrate systems have been studied in melts by the conductance method, which was evidently inadequate, since many authors [3, 4, 5] have repeatedly returned to certain of these indicated systems.

EXPERIMENTAL

The lithium nitrate-cadmium nitrate and sodium nitrate-cadmium nitrate systems described below were first investigated by the conductance method. The measurement of specific conductance was carried out in an apparatus assembled according to Kohlrausch with the substantial modifications described in the works of Belyaev and Mironov [6, 7].

The vessel for measuring the electrical conductance was calibrated with twice recrystallized, chemically pure, fused potassium nitrate. The numerical value for the conductance of potassium nitrate at various temperatures, which was necessary for determining the capacity of the vessel, was taken from Jaeger and Kapma [8]. The precision of the specific conductance measurements of the pure components was controlled by comparison of our data with the data of the above-named investigators.

The specific conductance was measured polythermally through a range of 5-8° and was calculated from the well-known formula: $\kappa = \frac{C}{R}$. Isotherms were constructed for the polytherms through a range of 20°. The values of the absolute and relative temperature coefficients were calculated for the isotherms obtained, respectively, from the formulas:

$$\alpha = \frac{\kappa_2 - \kappa_1}{t_2 - t_1} \quad \text{and} \quad \beta = \frac{\kappa_2 - \kappa_1}{t_2 - t_1} \cdot \frac{1}{\kappa_{av}}.$$

Binary System Cadmium Nitrate-Lithium Nitrate. The phase equilibrium diagram of the indicated system (state-temperature) has previously been described by one of us [1]. It consists of a simple eutectic. From the specific conductance measurements of the salt mixtures of the named components 19 polytherms were obtained, from the data of which seven isotherms were constructed: 200, 220, 240, 260, 280, 300, 320° (Fig. 1, Table 1). The system could not be investigated for compositions containing less than 15 equimolecular percent of cadmium nitrate. With lesser contents of the latter, decomposition of the melt is observed, accompanied by evolution of nitrogen dioxide.

Binary System Cadmium Nitrate-Sodium Nitrate. The composition-temperature equilibrium phase diagram of this system has been described previously [2] and also consists of a simple eutectic. The specific conductance of the binary mixtures was investigated in the temperature range of from 160 to 320°, and 19 polytherms were graphically drawn; by choosing points from these, 8 isotherms were constructed for the following temperatures: 180, 200, 220, 240, 260, 280, 300, 320° (Fig. 2, Table 2).

TABLE 1

Specific Conductance of Salt Mixtures in the System $\text{LiNO}_3\text{--Cd(NO}_3)_2$

Expt. No.	LiNO_3 (in equivalent molecular %)	Specific conductance κ at a temperature (in °) of							$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
		200	220	240	260	280	300	320	220-260°	260-300°	220-260°	260-300°
1	30	—	—	—	—	—	0.206	0.278	—	—	—	—
2	35	—	—	—	—	—	0.242	0.311	—	—	—	—
3	37.5	—	—	—	0.152	0.200	0.262	0.334	—	—	2.75	13.48
4	40.0	—	—	—	0.164	0.219	0.286	0.360	—	—	3.05	13.68
5	42.5	—	—	0.129	0.180	0.240	0.308	0.381	—	—	3.2	13.17
6	45.0	—	0.092	0.138	0.190	0.252	0.319	0.392	2.45	17.5	3.6	12.60
7	46.5	0.066	0.108	0.157	0.214	0.278	0.345	0.418	2.65	16.6	3.8	11.70
8	48.0	0.071	0.114	0.165	0.223	0.288	0.357	0.430	2.72	16.7	3.35	11.60
9	50	0.082	0.129	0.184	0.241	0.306	0.372	0.447	2.8	15.16	3.27	10.68
10	52.5	0.101	0.151	0.208	0.268	0.334	0.405	0.483	2.93	14.01	3.43	10.19
11	55	—	0.162	0.222	0.287	0.358	0.434	0.511	3.12	13.94	3.67	10.00
12	57.5	—	0.185	0.246	0.314	0.390	0.465	0.546	3.22	12.97	3.77	9.68
13	60.0	—	0.200	0.264	0.336	0.400	0.490	0.569	3.4	12.76	3.85	9.30
14	65	—	—	0.285	0.361	0.440	0.517	0.600	—	—	3.9	8.88
15	70	—	—	0.318	0.394	0.476	0.562	0.650	—	—	4.2	8.70
16	75	—	—	0.370	0.452	0.535	0.620	0.706	—	—	4.8	7.80
17	80	—	—	—	0.470	0.575	0.680	0.765	—	—	5.25	9.10
18	90	—	—	—	0.567	0.690	0.810	0.925	—	—	6.07	7.50
19	100	—	—	—	0.795	0.930	1.070	1.210	—	—	—	—

TABLE 2

Specific Conductance of Salt Mixtures in the System $\text{NaNO}_3\text{--Cd(NO}_3)_2$

Expt. No.	NaNO_3 (in equivalent molecular %)	Specific conductance κ at a temperature (in °) of								$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
		180	200	220	240	260	280	300	320	220-260°	260-300°	220-260°	260-300°
1	25	—	—	—	—	0.105	0.1495	0.195	0.245	—	—	2.25	15.07
2	30	—	0.032	0.053	0.088	0.132	0.1795	0.230	0.279	1.9	20.65	2.45	13.55
3	32.5	0.021	0.042	0.073	0.115	0.154	0.205	0.257	0.307	2.02	17.90	2.57	12.52
4	34	0.025	0.047	0.083	0.120	0.167	0.218	0.269	0.319	2.12	17.20	2.55	11.70
5	36	0.028	0.055	0.093	0.132	0.180	0.230	0.284	0.335	2.18	16.15	2.60	11.20
6	37.5	0.031	0.058	0.097	0.141	0.187	0.240	0.292	0.346	2.25	15.90	2.62	10.90
7	40	0.043	0.073	0.115	0.158	0.208	0.263	0.315	0.369	2.30	14.40	2.68	10.19
8	42.5	0.045	0.080	0.125	0.176	0.227	0.283	0.336	0.390	2.57	14.60	2.70	9.66
9	45	0.055	0.090	0.136	0.190	0.243	0.302	0.360	0.416	2.70	14.24	2.90	9.59
10	47.5	0.061	0.096	0.148	0.203	0.259	0.320	0.382	0.446	2.77	13.67	3.10	9.48
11	50	—	0.111	0.160	0.219	0.278	0.343	0.406	0.470	2.98	13.56	3.20	9.33
12	52.5	—	—	0.180	0.243	0.307	0.374	0.442	0.510	3.18	13.03	3.38	9.01
13	55	—	—	—	0.266	0.324	0.389	0.460	—	—	—	3.40	8.69
14	57.5	—	—	—	0.284	0.354	0.424	0.485	0.564	—	—	3.30	7.80
15	60	—	—	—	0.306	0.378	0.449	0.521	0.592	—	—	3.60	7.90
16	65	—	—	—	—	0.408	0.488	0.568	0.646	—	—	4.00	8.19
17	70	—	—	—	—	0.458	0.537	0.614	0.692	—	—	3.90	7.27
18	80	—	—	—	—	—	0.634	0.735	0.792	—	—	—	—
19	100	—	—	—	—	—	—	—	0.920	—	—	—	—

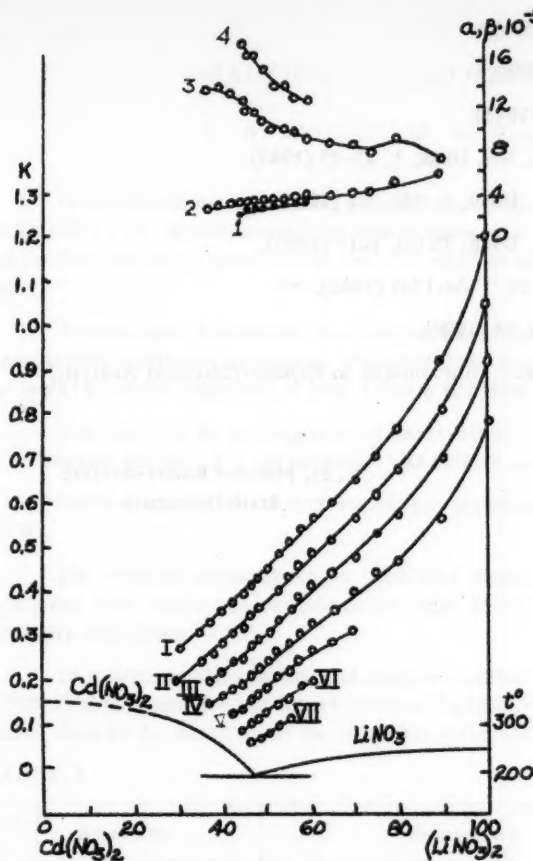


Fig. 1. Specific conductance isotherms and temperature coefficients of the binary system consisting of the nitrates of cadmium and lithium. Temperature coefficients: Absolute: 1) 220-260°; 2) 260-300°; Relative: 3) 260-300°; 4) 220-260°. Isotherms: I) 320°; II) 300°; III) 280°; IV) 260°; V) 240°; VI) 220°; VII) 200°.

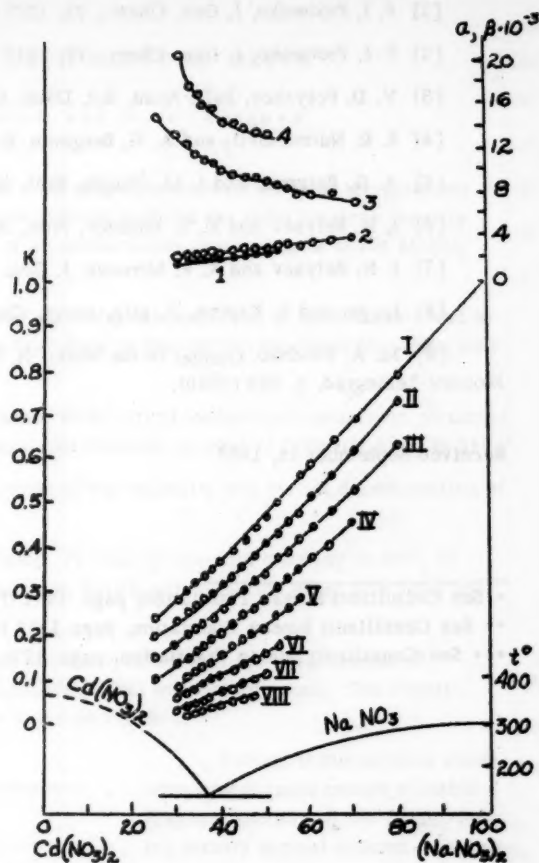


Fig. 2. Isotherms of specific conductance and temperature coefficients of binary systems consisting of the nitrates of cadmium and of sodium. Temperature coefficients: Absolute: 1) 220-260°; 2) 260-300°; Relative: 3) 260-300°; 4) 220-260°. Isotherms: I) 320°; II) 300°; III) 280°; IV) 260°; V) 240°; VI) 220°; VII) 200°; VIII) 180°.

The absence of chemical reaction in the melts between cadmium nitrate on the one hand and lithium nitrate and sodium nitrate on the other hand was established by us from the composition-temperature equilibrium phase diagrams of the systems [1, 2], which was also quite convincingly confirmed by the form of the conductance isotherms and of the absolute and relative temperature coefficient curves. According to M. A. Kłochko's classification [9], we have here the "third type" of conductance in binary systems, i.e., a case in which the conductance regularly increases from the more poorly conducting component, cadmium nitrate to the better conducting nitrates of lithium and sodium.

SUMMARY

1. The conductance of binary mixtures consisting of cadmium nitrate-lithium nitrate and cadmium nitrate-sodium nitrate in melts was investigated.
2. It was shown that the conductance isotherms increase almost rectilinearly in the melts from the more poorly conducting cadmium nitrate to the better conducting nitrates of lithium and of sodium.
3. It was confirmed that in melts, lithium nitrate and sodium nitrate do not react chemically with cadmium nitrate.

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- * See Consultants Bureau Translation, page 1351 ff.
- ** See Consultants Bureau Translation, page 1357 ff.
- *** See Consultants Bureau Translation, page 1775 ff.

REACTION OF LEAD TITANATE WITH SALTS IN MELTS

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Lead titanate has interesting piezoelectric properties over a broad temperature range up to temperatures above 500° [1-5]. In this connection lead titanate is of exceptional interest both for the radio ceramics industry and for the elucidation of the nature and treatment of the theory of piezoelectricity in compounds of the MeXO_3 type.

A great deal of attention has been paid by physicists to the piezoelectric properties of lead titanate and to piezoelectric substances in general, while too little attention has been paid to this subject by chemists. Thus, only one work [6] on the chemistry of lead titanate is known to us.

The results of an investigation of the reaction of lead titanate with salts of monovalent metals are presented in the present article. The investigation was carried out by a visual-polythermal method of fusibility of up to 1100°.

Further increase of the temperature was impossible on account of the volatility and partial decomposition of PbTiO_3 .

The reagents necessary for the work were prepared as follows: PbTiO_3 by two-fold sintering at 900°, of PbCO_3 and TiO_2 , taken in a stoichiometric ratio; KVO_3 by fusion of c.p. K_2CO_3 and V_2O_5 ; the other salts were analytically pure grade.

13 systems in all, consisting of diagonal sections of ternary mutual systems with the participation of PbTiO_3 (Table 1) and the two binary systems Na_2MoO_4 - PbO and Na_2WO_4 - PbO were investigated. The experimental data on the fusibility of the systems is presented in Table 2 and on Figs. 1-4.

TABLE 1

Expt. No.	System	Reaction
1	$\text{Na, Pb} \parallel \text{SiO}_3, \text{TiO}_3$	$\text{Na}_2\text{SiO}_3 + \text{PbTiO}_3 \leftarrow \text{Na}_2\text{TiO}_3 + \text{PbSiO}_3$
2	$\text{K, Pb} \parallel \text{SiO}_3, \text{TiO}_3$	$\text{K}_2\text{SiO}_3 + \text{PbTiO}_3 \leftarrow \text{K}_2\text{TiO}_3 + \text{PbSiO}_3$
3	$\text{K, Pb} \parallel \text{F, TiO}_3$	$\text{K}_2\text{F}_2 + \text{PbTiO}_3 \leftarrow \text{K}_2\text{TiO}_3 + \text{PbF}_2$
4	$\text{Na, Pb} \parallel \text{F, TiO}_3$	$\text{Na}_2\text{F}_2 + \text{PbTiO}_3 \leftarrow \text{Na}_2\text{TiO}_3 + \text{PbF}_2$
5	$\text{K, Pb} \parallel \text{VO}_3, \text{TiO}_3$	$\text{K}_2(\text{VO}_3)_2 + \text{PbTiO}_3 \leftarrow \text{K}_2\text{TiO}_3 + \text{Pb}(\text{VO}_3)_2$
6	$\text{Na, Pb} \parallel \text{VO}_3, \text{TiO}_3$	$\text{Na}_2(\text{VO}_3)_2 + \text{PbTiO}_3 \leftarrow \text{Na}_2\text{TiO}_3 + \text{Pb}(\text{VO}_3)_2$
7	$\text{K, Pb} \parallel \text{CO}_3, \text{TiO}_3$	$\text{K}_2\text{CO}_3 + \text{PbTiO}_3 \leftarrow \text{K}_2\text{TiO}_3 + \text{PbCO}_3$
8	$\text{Na, Pb} \parallel \text{CO}_3, \text{TiO}_3$	$\text{Na}_2\text{CO}_3 + \text{PbTiO}_3 \leftarrow \text{Na}_2\text{TiO}_3 + \text{PbCO}_3$
9	$\text{Na, Pb} \parallel \text{MoO}_4, \text{TiO}_3$	$\text{Na}_2\text{MoO}_4 + \text{PbTiO}_3 \leftarrow \text{Na}_2\text{TiO}_3 + \text{PbMoO}_4$
10	$\text{Na, Pb} \parallel \text{WO}_4, \text{TiO}_3$	$\text{Na}_2\text{WO}_4 + \text{PbTiO}_3 \leftarrow \text{Na}_2\text{TiO}_3 + \text{PbWO}_4$
11	$\text{K, Pb} \parallel \text{MoO}_4, \text{TiO}_3$	$\text{K}_2\text{MoO}_4 + \text{PbTiO}_3 \leftarrow \text{K}_2\text{TiO}_3 + \text{PbMoO}_4$
12	$\text{K, Pb} \parallel \text{P}_2\text{O}_7, \text{TiO}_3$	$\text{K}_4\text{P}_2\text{O}_7 + (\text{PbTiO}_3)_2 \leftarrow 2\text{K}_2\text{TiO}_3 + \text{Pb}_2\text{P}_2\text{O}_7$
13	$\text{Na, Pb} \parallel \text{P}_2\text{O}_7, \text{TiO}_3$	$\text{Na}_4\text{P}_2\text{O}_7 + (\text{PbTiO}_3)_2 \leftarrow 2\text{Na}_2\text{TiO}_3 + \text{Pb}_2\text{P}_2\text{O}_7$

Eleven of the sections which were investigated consist of stable diagonal sections of the corresponding ternary mutual systems. The sections for the fluorides, silicates, molybdates and tungstates of sodium and potassium with lead titanate belong to this class. Lead titanate dissolves rather well in melts of sodium and potassium fluorides and silicates. Thus, the solubility of lead titanate in sodium silicate reaches 50% at 1000°. In the diagonal section K_2SiO_3 - PbTiO_3 the lead titanate branch in the interval from 35% PbTiO_3 at 706° to 51% PbTiO_3 at 726° apparently intersects the field of the chemical compound formed within the reciprocal system. The PbTiO_3

branch in the $(\text{NaVO}_3)_2$ - PbTiO_3 section in the interval under investigation apparently intersects two fields, also of chemical compounds.

Particular interest attaches to the diagonal sections Na_2F_2 - PbTiO_3 , Na_2MoO_4 - PbTiO_3 , Na_2WO_4 - PbTiO_3 . Stratification occurs in these three systems - in all cases lead titanate crystallizes under the region of stratification. On the curve Na_2F_2 - PbTiO_3 the interval of stratification is from 2 to 20% PbTiO_3 , on the curve Na_2MoO_4 - PbTiO_3 from 1.5 to 3.5% PbTiO_3 and in the case Na_2WO_4 - PbTiO_3 , the stratification exists only in the interval from 1.25 to 2.25% PbTiO_3 . In the system Na_2F_2 - PbTiO_3 , where the interval of stratification is rather broad (18%) we can establish that the crystallization of PbTiO_3 under the region of stratification does not proceed in the triphasic monotectic process (Fig. 1), characteristic of stable diagonal sections of ternary systems.

* The percentages are equimolecular throughout.

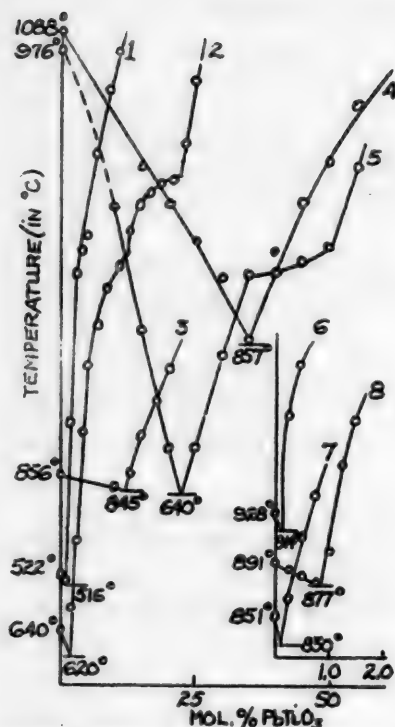


Fig. 1. Fusion curves of stable diagonal sections.
1) $(KVO_3)_2$, 2) $(NaVO_3)_2$, 3) K_2F_2 , 4) Na_2SiO_3 , 5) K_2SiO_3 , 6) K_2MoO_4 , 7) Na_2CO_3 , 8) K_2CO_3 . The second component is $PbTiO_3$.

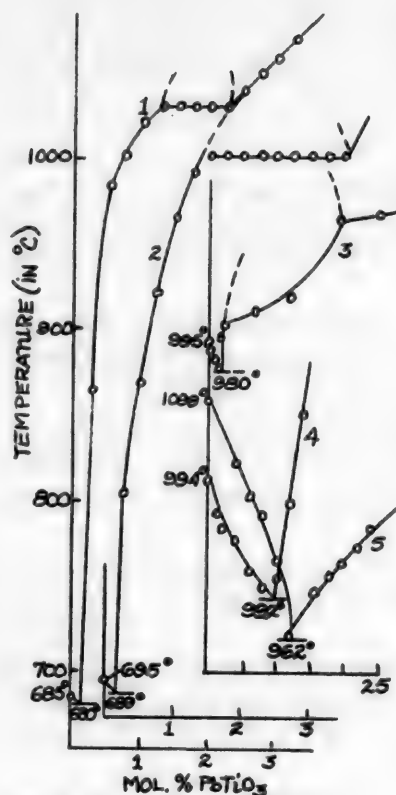


Fig. 2. Fusion curves of diagonal sections.
1) Na_2WO_4 , 2) Na_2MoO_4 , 3) Na_2F_2 , 4) $Na_4P_2O_7$, 5) $K_4P_2O_7$. The second component is $PbTiO_3$.

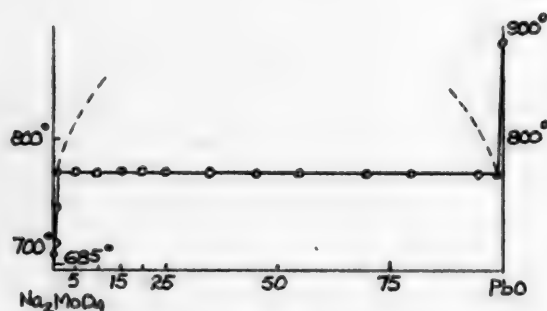


Fig. 3. Fusibility of the binary system Na_2MoO_4 - PbO .

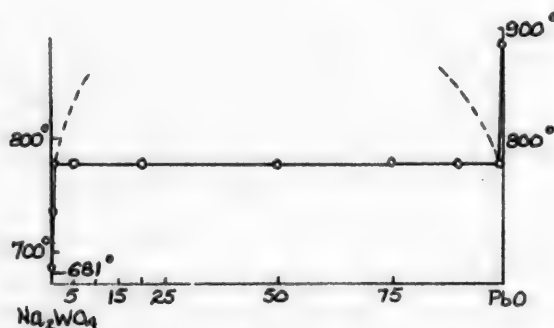


Fig. 4. Fusibility of the binary system Na_2WO_4 - PbO .

As has been shown by one of us, the stratification arising in the diagonal sections set forth is the result of the intrusion of two liquid phases with side faces of more complex three dimensional diagrams (prisms, tetrahedra), representing the diagrams of four component systems respectively of six (Na , Pb , Ti || O , F) and four components (Na_2O , PbO , $(W)MoO_3$, TiO_2).

The tertiary reciprocal systems Na , Pb || WO_4 , TiO_3 ; Na , Pb || F , TiO_3 and Na , Pb || MoO_4 , TiO_3 , on the stable diagonal sections of which (Na_2F_2 - $PbTiO_3$; Na_2MoO_4 - $PbTiO_3$; Na_2WO_4 - $PbTiO_3$) stratification was detected consisting of the elements (intersecting) of the above-mentioned three-dimensional diagrams of four component systems. The systems Na_2F_2 - PbO , Na_2WO_4 - PbO , Na_2MoO_4 - PbO , investigated in detail by us, (Fig. 3, 4) appear to be the intersecting side faces of these figures. Here stratification exists, occupying almost the entire composition

region; the liquid layers of these intersections are displayed on the diagonal sections Na_2F_2 - $PbTiO_3$, Na_2MoO_4 - $PbTiO_3$, Na_2WO_4 - $PbTiO_3$. Thus, of the two liquid phases on the stable diagonal sections of the ternary reciprocal

TABLE 2

Column 1 - % PbTiO₃; Column 2 - Temperature at which the first crystals appeared.
(E - Eutectic, P - Intersection of the branches of crystallization)

1	2	1	2	1	2	1	2
(NaVO ₃) ₂ —PbTiO ₃		Na ₂ WO ₄ —PbTiO ₃		K ₂ SiO ₃ —PbTiO ₃		From 0.5 to 99.75% 778°	
0	640	0	685	10	854	100	886
1	620	0.25	865	15	764	E at 681° and 0.1% PbO	
2	655	0.5	985	20	675	(KVO ₃) ₂ —PbTiO ₃	
3	705	0.75	1004	25	675	0	522
4	787	1	1022	30	747	1	516
5	836	1.25	1032	40	806	2	634
7	868	1.5	1032	45	816	3	744
9	895	1.75	1032	50	825	4	762
11	912	2	1032	55	886	5	773
13	938	2.25	1032	E at 640° and 22.5% PbTiO ₃		7	836
15	957	2.5	1042	Na ₂ MoO ₄ —PbTiO ₃		9	884
17	967	2.75	1050	0	895	11	912
19	975	3	1061	0.25	805	E at 516° and 1% PbTiO ₃	
21	977	3.25	1070	0.5	870	K ₂ MoO ₄ —PbTiO ₃	
23	1004	E at 680° and 0.2% PbTiO ₃		0.75	922	0	928
25	1050	Na ₂ F ₂ —PbTiO ₃		1	967	0.25	1000
E at 620° and 1% PbTiO ₃		0	995	1.25	995	0.5	1040
K ₄ P ₂ O ₇ —(PbTiO ₃) ₂		0.25	994	1.5	1004	E at 914° and 0.12% PbTiO ₃	
0	1099	0.5	989	1.75	1004	K ₂ F ₂ —PbTiO ₃	
4	1061	0.75	985	2	1004	0	856
6	1043	1	982	2.25	1004	10	847
8	1032	1.5	980	2.5	1004	13	897
10	1004	1.75	997	2.75	1004	15	885
12	962	2	1004	3	1004	18	911
16	988	7	1012	3.25	1004	20	935
18	998	12	1021	3.5	1004	E at 845° and 12% PbTiO ₃	
20	1005	19	1065	3.75% did not dissolve up to 1100°		K ₂ CO ₃ —PbTiO ₃	
22	1014	25	1070	E at 689° and 0.2% PbTiO ₃		0	891
24	1025	E at 980° and 1.5% PbTiO ₃		Na ₂ MoO ₄ —PbO		0.25	884
P at 962° and 12.5% PbTiO ₃		Na ₂ SiO ₃ —PbTiO ₃		0% PbO	695	0.5	880
Na ₄ P ₂ O ₇ —(PbTiO ₃) ₂		0	1088	0.25	704	0.75	877
0	994	15	985	0.5	737	1	900
1	975	20	957	From 0.75 % to 99.75 % 769°		1.25	965
2	964	25	930	100 886		1.5	998
4	958	30	904	E at 685° and 0.2% PbO		E at 877° and 0.75% PbTiO ₃	
6	940	35	857	Na ₂ WO ₄ —PbO		Na ₂ CO ₃ —PbTiO ₃	
8	930	40	924	0% PbO	685	0	851
10	936	45	960	0.25	737	0.25	865
12	980	50	991	E at 830° and 0.15% PbTiO ₃		0.5	912
14	1032	55	1031			0.75	942
P at 922° and 9% PbTiO ₃		E at 857° and 35% PbTiO ₃					

systems under consideration, only one consists of components of a stable pair of salts ($\text{Na}_2\text{F}_2-\text{PbTiO}_3$, $\text{Na}_2\text{MoO}_4-\text{PbTiO}_3$, $\text{Na}_2\text{WO}_4-\text{PbTiO}_3$); the other phase consists of PbO obtained by decomposition of PbTiO_3 under the influence of NaF , Na_2WO_4 , Na_2MoO_4 . Both phases were enriched by the decomposition product $\text{PbTiO}_3-\text{TiO}_2$.

The experimental material set forth confirms the correctness of the views propounded concerning the nature of stratification in ternary reciprocal systems.

It follows from the data obtained that lead titanate, in the character of its reaction with various salts, has much in common with barium titanate [7], and differs from barium titanate only in a considerably better solubility in fused salts, which is probably associated with the lower melting point of PbTiO_3 due to the greater polarizability and polarizing action of the Pb^{++} ion in comparison with the Ba^{++} ion.

SUMMARY

1. The fusion diagrams of lead titanate with the fluorides, silicates, pyrophosphates, molybdates, tungstates and carbonates of sodium and potassium were investigated up to 1100° .

2. It was established that lead titanate forms eutectic systems with melts of the fluorides, silicates, carbonates, molybdates, tungstates of sodium and potassium. The eutectic systems can be utilized for cultivating monocrystals of lead titanate from the fused media.

3. A great analogy in chemical properties of lead titanate and barium titanate was established.

4. The fusion diagrams of $\text{Na}_2\text{WO}_4-\text{PbO}$ and $\text{Na}_2\text{MoO}_4-\text{PbO}$ were investigated.

5. It was confirmed that stratification in the stable diagonal sections $\text{Na}_2\text{F}_2-\text{PbTiO}_3$, $\text{Na}_2\text{WO}_4-\text{PbTiO}_3$, $\text{Na}_2\text{MoO}_4-\text{PbTiO}_3$ arises due to the intrusion of two liquid phases with side faces of three-dimensional diagrams of four component systems.

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BEHAVIOR OF MAGNESIUM IN ALKALINE SOLUTIONS

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The position of magnesium in the electrochemical potential series is due to its considerable chemical activity in aqueous solutions of electrolytes. Passivity of magnesium can be observed only in alkaline solutions as well as in solutions of fluorides and chromates. Those solutions are used in technology to create coatings which protect magnesium and its alloys from corrosion.

The capacity of magnesium to become passive in alkaline solutions was noted for the first time by Kistya-kovsky [1]. The behavior of magnesium in alkaline solutions was apparently not studied in greater detail. Shilov and Shatunovskaya [2] observed the behavior of magnesium in distilled water at temperatures of 25 and 40°. Under these conditions the rate of reaction between magnesium and water falls with time, while the formation of a protective film is observed on the surface of the metal.

The formation conditions of protective films on magnesium in alkaline solutions at raised temperatures were studied in the present work.

EXPERIMENTAL

Pure magnesium (99.96%) was used for the experiments. The experiments were carried out with cylindrical shaped samples. The surface of a single sample was equal to 30 cm².

The acidification of magnesium in alkaline solutions both at room temperature and at raised temperatures was accompanied by vigorous evolution of hydrogen, particularly in the initial stage of the process. The gas evolution considerably decreased with the passage of time. At the same time a compact protective film, having various interference colors depending on its thickness, was formed on the metal.

The question of the chemical nature of the protective films formed on magnesium in alkaline solutions had not been resolved until very recently. Electronographic study indicated that it consists of a hydrate of magnesium oxide having a simple hexagonal lattice in which $a = 3.13 \text{ \AA}$ and $c = 4.75 \text{ \AA}$. The electronograms were taken by reflecting beams from the surface of samples covered with the oxide film. It should be indicated that on heating in air a film of magnesium oxide forms on magnesium which has a cubic structure of the sodium chloride type with a lattice constant $a = 4.20 \text{ \AA}$.

The kinetics of the growth of the protective film was studied under various operating conditions. To this end the weight of the films was determined at various stages of their growth by means of eliminating the films from the metal samples in a 20% solution of chromic anhydride; this dissolves the magnesium oxide and is practically without action on the metal. The samples were kept in the chromic anhydride solution for 30 seconds at room temperature. In the course of this time the change in the weight of the sample as a consequence of the solution of the metal itself amounted to 0.3 - 0.5 mg. With a film weight of 5 - 10 mg the error in the determination did not exceed 10%. The reproducibility of the experiments was of the same order of magnitude. The thickness of the film could be evaluated from its weight, taking its specific gravity as equal to the specific gravity of brucite ($\gamma = 2.40$) [3]. The total quantity of oxidized metal was also determined, excluding the weight of the films, as the difference between the weight of the samples of the metal before oxidation and after elimination of the films.

The corresponding weights of the films and the quantity of oxidized metal (in milligrams) depending on the time during which the alkaline solution acted on the metal are set forth in Figs. 1 and 2. The solution contained 810 g/liter of sodium hydroxide. The experiments were conducted at various temperatures from 20° to the temperature at which the solution boiled (135°). On the right hand side of the ordinate in Fig. 1 are placed the values of the thickness of the films (in microns).

Comparable data for the solution containing 1065 g/liter of sodium hydroxide are set forth in Figs. 3 and 4. In this case formation of a loose precipitate of magnesium oxide hydrate located on top of the compact film was observed at a temperature of 145°.

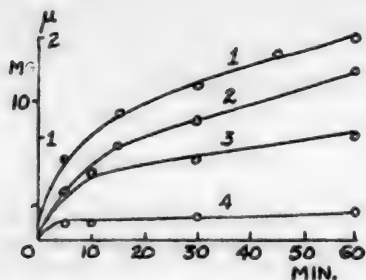


Fig. 1. Growth of the protective film on magnesium at various temperatures. The solution contained 810 g/liter of sodium hydroxide. 1) 135°; 2) 120°; 3) 105°; 4) 20°.

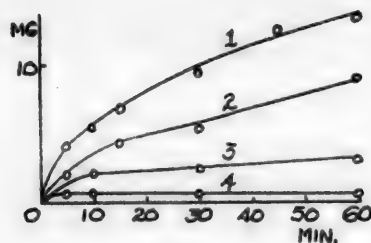


Fig 2. Quantity of metal oxidized as a function of the temperature of the solution. The solution contained 810 g/liter of sodium hydroxide. 1) 135°; 2) 120°; 3) 105°; 4) 20°.

Thus, by raising the temperature of the alkaline solution, the weight of the film and the quantity of metal oxidized was considerably increased. The formation of a protective film inhibits the chemical reaction between metal and solution, which initially occurred rather vigorously. The curves which characterize the change in the quantity of metal oxidized as a function of the time are close to parabolas.

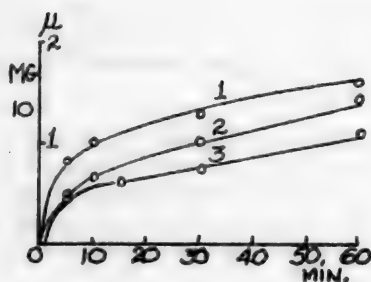


Fig. 3. Growth of the protective film on magnesium at various temperatures. The solution contained 1065 g/liter of sodium hydroxide. 1) 145°; 2) 120°; 3) 105°.

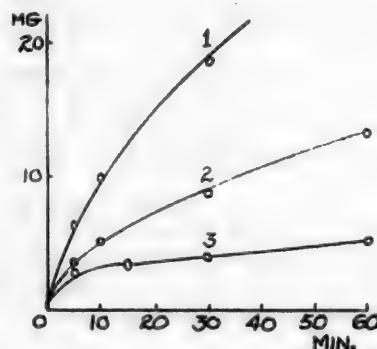


Fig. 4. Quantity of metal oxidized as a function of the temperature of the solution. The solution contained 1065 g/liter of sodium hydroxide. 1) 145°; 2) 120°; 3) 105°.

Since the composition of the film is known, the weight of metal in it can be calculated. The calculations show that a considerable quantity of metal goes over into solution in the process of growth of the protective film. This is illustrated by the data of Fig. 5.

Changing the rate of stirring the solution from 30 to 100 revolutions per minute did not substantially influence the kinetics of the growth of the film. The weight of the film which was formed was also not dependent on the introduction of oxidant into the alkaline solution.

At all stages of the growth of the film of magnesium oxide hydrate, it evidently remained permeable to water and alkaline solutions. The rate of the oxidation of the metal is regulated by diffusion phenomena and depends on the thickness of the protective film being formed. To a considerable extent it depends on the temperature of the solution, and to a lesser degree on the concentration of alkali. During simultaneous increase in the concentration of alkali and of the temperature of the solution, the quantity of metal oxidized appreciably increases, and loosening of the oxide film being formed is observed. This is probably associated with intensification of peptization of magnesium oxide hydrate.

SUMMARY

1. Compact protective films consisting of magnesium oxide hydrate are formed on magnesium in concentrated alkaline solutions at increased temperatures.

2. The process of film growth is self limiting. The rate of growth considerably increases with increased temperature of the solution, and to a lesser degree increases with increasing concentration of alkali.

3. The experiments carried out make it possible to establish the conditions for obtaining films with maximum protective capacity. Compact films with a thickness of about $2\ \mu$ can be obtained by treating magnesium with solutions containing 700-800 g/liter of sodium hydroxide at the boiling temperature (130-135°). Protective films on magnesium and its alloys consisting of magnesium hydroxide are of interest from a practical point of view.

In conclusion, I consider it my duty to express my gratitude to Professor A. G. Samartsev for his long-standing interest in the present work.

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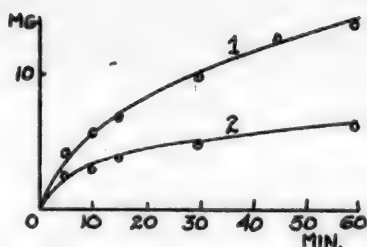


Fig. 5. Oxidation of magnesium in a solution containing 810 g/liter of sodium hydroxide at a temperature of 135°. 1) Total quantity of metal oxidized; 2) quantity of metal in the surface film of magnesium oxide hydrate.

REACTION OF BARIUM TITANATE WITH SALTS IN MELTS

M. L. Sholokhovitch and I. N. Belyaev

The necessity of investigating the reaction of barium titanate dissolved in melts consisting of various substances with those substances, in relation to its exceptionally interesting piezoelectric properties has been noted in the preceding works [1-3]. In the present article, the results of investigations of the reaction of barium titanate with fluorides, silicates, carbonates, pyro- and metaphosphates, metaborates, chlorides, molybdates, tungstates and other salts of the alkaline, and of certain divalent metals in the fused state are set forth. The investigation was carried out up to a temperature of 1200° by a visual-polythermal method.

The salts necessary for the present investigation were prepared as follows: BaTiO₃ by two-fold sintering at 1200° of a mixture of BaCO₃ and TiO₂ in a stoichiometric ratio; KVO₃, Pb(PO₃)₂, Pb₃(PO₄)₂ and Pb(BO₂)₂ via fusion of chemically pure K₂CO₃ and V₂O₅, PbO and NH₄H₂PO₄, PbO and B₂O₃, taken in stoichiometric ratios; NaPO₃, KPO₃ and K₄P₂O₇ by roasting chemically pure NaH₂PO₄, KH₂PO₄ and K₂HPO₄. The other salts used were chemically pure or analytically pure grade, preliminarily recrystallized.

TABLE 1

Expt. No.	System	Reaction
1	Na, Ba F, TiO ₃	2NaF + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaF ₂
2	K, Ba F, TiO ₃	2KF + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + BaF ₂
3	Li, Ba F, TiO ₃	2LiF + BaTiO ₃ \rightleftharpoons Li ₂ TiO ₃ + BaF ₂
4	Na, Ba Cl, TiO ₃	2NaCl + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaCl ₂
5	K, Ba Cl, TiO ₃	2KCl + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + BaCl ₂
6	Li, Ba Cl, TiO ₃	2LiCl + BaTiO ₃ \rightleftharpoons Li ₂ TiO ₃ + BaCl ₂
7	Na, Ba SO ₄ , TiO ₃	Na ₂ SO ₄ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaSO ₄
8	K, Ba SO ₄ , TiO ₃	K ₂ SO ₄ + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + BaSO ₄
9	Li, Ba SO ₄ , TiO ₃	Li ₂ SO ₄ + BaTiO ₃ \rightleftharpoons Li ₂ TiO ₃ + BaSO ₄
10	Na, Ba MoO ₄ , TiO ₃	Na ₂ MoO ₄ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaMoO ₄
11	K, Ba MoO ₄ , TiO ₃	K ₂ MoO ₄ + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + BaMoO ₄
12	Na, Ba WO ₄ , TiO ₃	Na ₂ WO ₄ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaWO ₄
13	Na, Ba PO ₃ , TiO ₃	2NaPO ₃ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + Ba(PO ₃) ₂
14	K, Ba PO ₃ , TiO ₃	2KPO ₃ + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + Ba(PO ₃) ₂
15	Pb, Ba PO ₃ , TiO ₃	Pb(PO ₃) ₂ + BaTiO ₃ \rightleftharpoons PbTiO ₃ + Ba(PO ₃) ₂
16	Pb, Ba PO ₄ , TiO ₃	Pb ₃ (PO ₄) ₂ + 3BaTiO ₃ \rightleftharpoons 3PbTiO ₃ + Ba ₃ (PO ₄) ₂
17	Na, Ba P ₂ O ₇ , TiO ₃	Na ₄ P ₂ O ₇ + 2BaTiO ₃ \rightleftharpoons 2Na ₂ TiO ₃ + Ba ₂ P ₂ O ₇
18	K, Ba P ₂ O ₇ , TiO ₃	K ₄ P ₂ O ₇ + 2BaTiO ₃ \rightleftharpoons 2K ₂ TiO ₃ + Ba ₂ P ₂ O ₇
19	Na, Ba VO ₃ , TiO ₃	2NaVO ₃ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + Ba(VO ₃) ₂
20	K, Ba VO ₃ , TiO ₃	2KVO ₃ + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + Ba(VO ₃) ₂
21	Na, Ba SiO ₃ , TiO ₃	Na ₂ SiO ₃ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaSiO ₃
22	K, Ba SiO ₃ , TiO ₃	K ₂ SiO ₃ + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + BaSiO ₃
23	Li, Ba SiO ₃ , TiO ₃	Li ₂ SiO ₃ + BaTiO ₃ \rightleftharpoons Li ₂ TiO ₃ + BaSiO ₃
24	Na, Ba CO ₃ , TiO ₃	Na ₂ CO ₃ + BaTiO ₃ \rightleftharpoons Na ₂ TiO ₃ + BaCO ₃
25	K, Ba CO ₃ , TiO ₃	K ₂ CO ₃ + BaTiO ₃ \rightleftharpoons K ₂ TiO ₃ + BaCO ₃
26	Pb, Ba BO ₂ , TiO ₃	Pb(BO ₂) ₂ + BaTiO ₃ \rightleftharpoons PbTiO ₃ + Ba(BO ₂) ₂

26 systems in all were investigated, consisting of diagonal sections of ternary reciprocal systems with the participation of barium titanate. These systems are set forth in Table 1, in the left portion of the equations. The two binary systems: BaTiO₃ with BaCl₂ and Na₂TiO₃ were also investigated. The fusion data and character of the crystals formed permitted us to establish that 19 of the 26 systems investigated were stable diagonal sections of reciprocal systems. This means that there is no exchange reaction between the components. The experimental data concerning the fusibility of the systems (the solubility of BaTiO₃ at various temperatures) are set forth in Table 2.

The very low content (percentages up to 7-8%) of BaTiO₃ in the eutectic compositions appears to be characteristic of stable diagonal sections with barium titanate. (The systems Li₂SiO₃-BaTiO₃ and Na₂SiO₃-BaTiO₃ where respectively 16 and 27% BaTiO₃ enter into the composition of the eutectic mixtures, constitute an exception).

This is evidence that the exchange reaction of the indicated sections is markedly displaced in the direction of the starting materials. The latter also graphically illustrates the reciprocal systems Na, Ba || Cl, TiO₃ and Na, Ba || TiO₃, CO₃ previously investigated by us in which the field of BaTiO₃ occupies up to 99% of the entire area, while the isotherms intersection on the diagonal at an acute angle which even indicates a

* The fusion curves of BaTiO₃ with the silicates of sodium, potassium and lithium were obtained by G. A. Bukhalova.

TABLE 2

Column 1 — % BaTiO₃; Column 2 — Temperature at Which the First Crystals Appear. (E — Eutectic, P — Intersection of the branches of crystallization)

1	2	1	2	1	2	1	2
Na₂F₂-BaTiO₃		(KVO₃)₂-BaTiO₃		Na₂CO₃-BaTiO₃		Na₂SO₄-BaTiO₃	
0.0	982	0.0	520	0.0	857	0.70	990
0.5	975	0.5	508	0.25	852	1.00	up to 1200
1.0	971	1.0	500	0.50	844	(did not dissolve)	
3.0	967	1.5	559	0.75	840	E at 868° and 0.3% BaTiO ₃	
5.0	961	2.0	602	1.0	834	Li₂SO₄-BaTiO₃	
7.0	955	2.5	612	1.25	830	0.0	860
7.5	970	3.0	630	1.50	880	0.25	854
8.0	1000	3.5	659	1.75	980	0.50	900
8.5	1010	4.0	687	E at 826° and 1.4% BaTiO ₃		0.75	980
9.0	1023	5.0	712	K₂CO₃-BaTiO₃		1.0	up to 1000
11.0	1080	5.5	722	0.0	896	(did not dissolve)	
E at 952° and 7% BaTiO ₃		6.0	728	0.25	890	E at 849° and 0.4% BaTiO ₃	
K₂F₂-BaTiO₃		7.0	760	0.50	883	K₂MoO₄-BaTiO₃	
0.0	856	7.5	774	0.75	878	0.0	920
0.5	847	9.0	810	1.00	890	0.25	914
1.0	838	10.0	834	1.25	950	0.50	928
2.0	826	11.5	856	1.50	1000	0.75	984
3.0	818	14.0	900	1.75	up to 1100	1.00	1040
4.0	834	15.0	922	(did not dissolve)		E at 909° and 0.4% BaTiO ₃	
5.0	855	E at 500° and 1% BaTiO ₃		E at 873° and 0.9% BaTiO ₃		K₄P₂O₇-(BaTiO₃)₂	
6.0	894	Na₂SiO₃-BaTiO₃		(NaPO₃)₂-BaTiO₃		0.0	1099
6.5	920	0.0	1086	0.0	619	5.0	1060
7.0	932	3.0	1076	0.4	580	7.0	1042
7.5	960	6.0	1058	0.7	580	10.0	1022
8.0	974	9.0	1045	1.5	610	11.0	992
9.0	1000	14.0	1025	2.3	726	12.0	1004
10.0	1034	19.0	998	3.0	752	14.0	1020
12.0	1100	23.0	974	3.8	796	16.0	1040
E at 814° and 3.5% BaTiO ₃		25.0	958	4.5	830	20.0	1080
(NaVO₃)₂-BaTiO₃		29.0	969	6.0	850	22.0	1100
0.0	640	32.0	1016	E at 580° and 0.7% BaTiO ₃		P at 992° and 11% BaTiO ₃	
0.5	635	E at 942° and 27% BaTiO ₃		Pb(PO₃)₂-BaTiO₃		Na₄P₂O₇-(BaTiO₃)₂	
1.0	630	K₂SiO₃-BaTiO₃		0.0	616	0.0	994
2.0	620	0.0	976	0.25	616	0.5	992
2.5	611	2.0	934	0.50	614	1.0	989
3.0	625	4.0	922	1.0	630	1.6	979
3.5	668	6.0	958	1.5	662	2.0	969
4.0	720	9.0	988	2.0	708	2.5	959
4.6	752	12.0	1013	2.5	746	3.5	954
5.5	770	15.0	1028	3.0	780	4.5	948
6.0	780	20.0	1054	3.5	820	5.0	938
7.0	810	E at 900° and 3% BaTiO ₃		4.0	854	5.5	932
8.0	840	Li₂SiO₃-BaTiO₃		E at 613° and 0.7% BaTiO ₃		6.0	923
9.0	871	0.0	1200	Na₂SO₄-BaTiO₃		6.5	908
10.0	884	14.0	1100	0.0	885	7.0	897
11.0	904	16.0	1062	0.25	870	7.5	892
12.0	919	18.0	1072	0.50	940	8.5	888
13.0	930	20.0	1090				
14.0	939	E at 1048° and 16% BaTiO ₃					
16.0	960						
19.0	990						
E at 111° and 2.5% BaTiO ₃							

TABLE 2 (Continued)

1	2	1	2	1	2	1	2
$\text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$		$\text{Pb}(\text{BO}_2)_2 - \text{BaTiO}_3$		$(\text{KPO}_3)_2 - \text{BaTiO}_3$		$\text{Na}_2\text{WO}_4 - \text{BaTiO}_3$	
9.5	878	0.0	686	27.0	838	0.75	1028
11.0	868	2.0	658	28.0	858	1.0	1040
12.0	857	6.0	634	29.0	878	$\text{BaCl}_2 - \text{BaTiO}_3$	
13.0	857	10.0	588	30.0	898	0.0	964
13.5	867	15.0	752	31.0	918	0.25	960
14.0	888	20.0	816	33.0	943	0.50	955
14.5	903	25.0	870	33.5	960	0.75	945
15.0	918	30.0	925	35.0	990	1.0	941
15.5	953	35.0	970	P_1 at 746° and 11% BaTiO_3		1.25	936
16.0	974	P at 623° and 5% BaTiO_3		P_2 at 747° and 16% BaTiO_3		1.50	931
16.5	999	$(\text{KPO}_3)_2 - \text{BaTiO}_3$		P_3 at 776° and 24% BaTiO_3		1.75	926
17.0	1014	0.0	806	$\text{Na}_2\text{MoO}_4 - \text{BaTiO}_3$		2.0	924
18.0	1028	2.0	776	0.0	690	2.25	922
P at 853° and 13% BaTiO_3		4.0	760	0.25	683	2.5	920
$\text{Pb}_3(\text{PO}_4)_2 - (\text{BaTiO}_3)_3$		6.0	748	0.50	805	2.75	916
0.0	1014	7.0	747	0.75	900	3.0	919
0.5	1004	10.0	746	1.00	938	3.25	908
1.5	995	11.0	746	1.25	966	3.5	906
2.5	986	13.0	746	1.50	994	3.75	903
3.5	980	14.0	746	1.75 up to 1000		4.0	903
5.0	967	17.0	752	(did not dissolve)		4.25	922
6.5	968	18.0	756	P at 678° and 0.3% BaTiO_3		4.5	941
8.0	966	19.0	762	$\text{Na}_2\text{WO}_4 - \text{BaTiO}_3$		4.75	958
9.0	968	20.0	766	0.0	695	5.0	974
10.0	986	21.0	768	0.25	816	$\text{Na}_2\text{TiO}_3 - \text{BaTiO}_3$	
12.5	1014	22.0	772	0.50	980	0.0	1045
16.0	1040	23.0	776			1.0	1012
18.0	1056	24.0	786			2.0	1004
P at 623° and 9% BaTiO_3		25.0	802			3.0	996
		26.0	816			4.0	989
						5.0	1000
						6.0	1040

singular character for the systems. In connection with this the abrupt gradient of the branch of crystallization of BaTiO_3 is of interest in the stable sections under investigation; it is possible that, in the region of greatest concentrations of barium titanate and high temperatures, stratification of the components in the liquid state occurs. The systems formed by BaTiO_3 with the pyrophosphates of potassium and sodium, sodium tungstate, potassium metaphosphate, sodium molybdate, lead orthophosphate and metaborate do not appear to be stable sections of the corresponding reciprocal systems. The high fusion temperatures of the salts did not permit us to establish whether in these systems chemical compounds are formed or exchange products separate out.

The experimental material obtained indicates that barium titanate is a substance which is slightly soluble in the majority of salt melts. The best solvents (at $1000-1100^\circ$ from 6 to 40% of BaTiO_3 is dissolved) appear to be the silicates of lithium, sodium and potassium, the fluorides of sodium and potassium, potassium metaphosphate, sodium and potassium metavanadates, sodium and potassium pyrophosphates, lead orthophosphate and metaborate. The poorest solvents (at 1000° from 0.5 to 6% BaTiO_3 dissolved) appear to be carbonates of sodium, potassium and barium, and the metaphosphates of sodium and lead. Sodium sulfate and the molybdates of the alkaline metals are poor solvents (0.5 to 1.5% BaTiO_3 dissolved at 1000°). BaTiO_3 hardly dissolved at all (even in portions of tenths of a percent) in potassium sulfate, the chlorides of the alkali metals and in lithium fluoride.

It is evident from the data set forth that eutectic mixtures (Table 2) are formed in the majority of cases in diagonal sections of ternary reciprocal systems with the participation of barium titanate. This provides the possibility of utilizing the systems under study to select advantageous solvents for growing monocrystals of barium titanate from fused media.

It is practically and theoretically important to elucidate the general pattern of the reactions in reciprocal systems with the participation of barium titanate; with the aid of this it would be possible in advance to have a representation of the chemistry of the processes which proceed during the sintering of certain ceramic materials containing barium titanate and also concerning the solubility of barium titanate in various salt melts.

On account of the absence of data on the heat of formation of titanates, we cannot take advantage of the well-known rule which, in the absence of pronounced complex formation, makes it possible to judge the direction of the exchange reaction in reciprocal systems by the magnitude of the conventionally calculated heat effect of the reaction [4]. An attempt to extend to systems with the participation of barium titanate the Palkin's rule [5] to the effect that equilibrium in reciprocal systems is displaced in the direction of the most highly fusible component, and the rule of Gustavson-Beketov [6] concerning the tendency of the smaller ions to unite with the smaller and the larger, with the larger gives interesting results.

It turned out that Palkin's hypothesis and the Gustavson-Beketov rule applied very well to the majority of the systems which were studied. Thus, Palkin's hypothesis is quite justified for all systems which have a stable character and is not vindicated for systems on the fusion curves of which either exchange products, or chemical compounds arise [BaTiO_3 in combination with Na_2WO_4 , Na_2MoO_4 , $\text{Na}_4\text{P}_2\text{O}_7$, $\text{K}_4\text{P}_2\text{O}_7$, KPO_3 , $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}(\text{BO}_2)_2$]. Deviations from Palkin's thesis were also observed previously in a whole series of systems with sharply expressed complex formation, such as, for example: Li , $\text{K} \parallel \text{SO}_4$, PO_3 [7]; Li , $\text{K} \parallel \text{SO}_4$, NO_3 [8]; Li , $\text{Sr} \parallel \text{F}$, Cl ; Na , $\text{Ba} \parallel \text{F}$, Cl [9]; Li , $\text{Ba} \parallel \text{F}$, Cl [10]; Ca , $\text{Ba} \parallel \text{F}$, Cl [11] and others. This makes it possible to confirm that Palkin's thesis is generally applicable only to systems without complex formation or where the complex formation is slight. In accord with this, deviations from Palkin's rule in systems including BaTiO_3 are probably due to chemical reaction within the reciprocal systems.

Of the 26 sections investigated by us, only the systems BaTiO_3 with: $(\text{KPO}_3)_2$, $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}(\text{BO}_2)_2$, K_2MoO_4 , Na_2SO_4 , K_2SO_4 , Li_2SO_4 deviate from the Gustavson-Beketov rule. It is pertinent to note here that the direction of the exchange reaction found on the basis of the magnitude of the conventionally calculated heat effect often does not agree with the thesis of Palkin and the Gustavson-Beketov rule. This is characteristic in those cases in which chemical compounds are formed in the systems. The reaction $\text{Na}_2\text{Cl}_2 + \text{BaF}_2 = 2\text{NaF} + \text{BaCl}_2$ can serve as an example. According to Palkin's thesis and the conventionally calculated heat effect the equilibrium of the exchange reaction should be displaced toward $\text{Na}_2\text{Cl}_2 - \text{BaF}_2$; according to the Gustavson-Beketov rule, on the contrary, toward $\text{Na}_2\text{F}_2 - \text{BaCl}_2$. Actually the diagonal $\text{Na}_2\text{Cl}_2 - \text{BaF}_2$ intersects the field of a stable chemical compound $\text{BaCl}_2 \cdot \text{BaF}_2$.

It is noteworthy that of the 26 diagonal sections with the participation of BaTiO_3 , systems deviate from the thesis of Palkin in which participate an oxygen-containing anion, anions containing elements with incomplete electron shells (WO_4 , MoO_4), anions inclined toward polymerization (PO_3 , PO_4), and also cations with an 18 electron shell (Pb).

An attempt to extend to systems including barium titanate the recently proposed hypothesis to the effect that one of the factors facilitating the growth of irreversibility and consequently, the diminishing mutual solubility of salts of stable pairs, is the great difference in the polarizability of cations and anions [12], demonstrated that this hypothesis is justified only for the fluorides of the alkaline metals. BaTiO_3 is almost completely insoluble in lithium fluoride and is comparatively quite soluble in the fluorides of Na and K . This order of solubility is not observed in all the other systems, in spite of the fact that according to the polarizability of the ions: $\text{Li}-0.03$, $\text{Na}-0.19$, $\text{K}-0.89$, $\text{Ba}-1.86$, it should be observed in all cases. Analysis of the results obtained permits us to conclude as a first approximation that the solubilities of barium titanate in melts of various salts of Li , Na , K , and Pb are to a larger extent determined by the character of the anions than by that of the cations.

Inasmuch as the conventionally calculated thermal effect of the reaction is determined for room temperature, it cannot furnish a representation of the thermal effect of the reaction in the fused state; the fusion temperature of the salts and the radii of the ions cannot encompass every multiform system; they are justified only for the most simple systems consisting of ions with complete electron shells and not complicated with chemical reactions within the reciprocal system.

The solubility of the salts and the direction of the binary exchange reaction in the fused state are determined by the combination of a whole series of properties depending on the position of the elements in the Mendeleev periodic table (the structure of the inner electron shells, the polarizability, the radius of the ions, etc.). It appears to us that the character of the chemical bond in compounds most completely reflects the entire aggregation of properties of the elements; it is, therefore, necessary to take precisely this factor into account in the basic classification of reciprocal systems. Unfortunately, the quantitative evaluation of the character of the chemical bond is difficult for many compounds; none the less, it can be seen from the vast experimental material on the

solubility of salts in fused media and from exchange reactions that the equilibrium is always displaced in the direction of pairs of compounds which are markedly different from each other in the character of the chemical bond and the more marked this difference, the more the system will approach to the irreversible-singular type and the less will be the mutual solubility of salts of the stable pair. On the other hand, when the character of the bonds of the pair of salts is close, the system will always be reversible and the mutual solubility will be maximum. This conclusion is in excellent agreement with the long known rule: like dissolves in like.

Data concerning the solubility of barium titanate in various fused media are in excellent agreement with this: BaTiO_3 crystallizes in the perovskite pattern and consists of a continuous three dimensional anion consisting of regular or deformed (TiO_6) octahedra with a Ti ion in the center. Ba ions are located in the spaces between these octahedra [13]. In compounds of a similar type, for example PbTiO_3 , CaTiO_3 , SrTiO_3 and others, barium titanate not only dissolves in the fused state, but also yields solid solutions. The relatively good solubility of BaTiO_3 in silicates, metaphosphates and borates is, therefore, also comprehensible; it is characterized by the highly polymerized molecular structure.

The peculiar position which the fluorides of sodium and potassium occupy in the series of excellent solvents of barium titanate is of interest. Sodium and potassium fluorides crystallize in an ionic lattice of the NaCl type, and none the less appear to be some of the best solvents of BaTiO_3 , while BaTiO_3 is almost completely insoluble in the other halides of the alkaline metals. The excellent solubility of barium titanate in fluorides is apparently associated with partial substitution of oxygen ions by fluorine ions and, consequently, with weakening of the bond of titanium with oxygen.

SUMMARY

1. The fusion diagrams of barium titanate with fluorides, silicates, carbonates, pyro- and metaphosphates, metaborates, chlorides, molybdates, sulfates, tungstates of the alkaline and certain divalent metals were investigated up to 1200°.
2. It was established that of the 26 systems investigated, representing diagonal sections of ternary reciprocal systems, 19 were stable sections (Table 1) and can be utilized for cultivating monocrystals of BaTiO_3 from the fused media.
3. It was established that BaTiO_3 is poorly soluble in the majority of salt melts of Na, K, Li, Pb, and Ba.
4. It was shown that the character of the chemical bond as maximally reflecting the entire aggregate of properties of the elements, should be the basis for the classification of ternary reciprocal systems and of the theory of the solubility of salts in fused media.

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CRACKING OF NORMAL PARAFFINIC HYDROCARBONS IN THE PRESENCE OF

ALUMINUM CHLORIDE

I. CRACKING OF n-HEPTANE AND n-NONANE

L. A. Potolovsky and G. S. Spektor

The object of the present work is to study the influence of the magnitude of the molecular weight of the initial normal paraffinic hydrocarbon and the conditions of cracking in the presence of aluminum chloride on the composition of the end products of the cracking, and to specify the composition of these products.

A considerable amount of work has been devoted to the cracking of individual low molecular weight paraffinic hydrocarbons of normal structure in the presence of aluminum chloride. The action of halogen salts of aluminum on paraffinic hydrocarbons of normal structure was studied for the first time by Gustavson in 1881 [1, 2]. Moldavsky [3-6] and also other investigators [7-14] conducted significant investigations in this field. As a result of the study of the cracking of individual normal paraffinic hydrocarbons from C_6 to C_8 in the presence of $AlCl_3$ at atmospheric pressure and at temperatures not exceeding the boiling point of the initial hydrocarbons, it was established that the basic reaction products formed were iso-paraffinic hydrocarbons with both less and greater numbers of carbon atoms in the molecule than in the initial hydrocarbon, and also isomers of the latter. Naphthenic, aromatic and unsaturated hydrocarbons were absent in the reaction products (in the hydrocarbon layer, not bound to $AlCl_3$).

In the work [15-18] on the cracking of normal paraffinic hydrocarbons with a carbon atom content of C_9 and up, the products formed as a result of the reaction have hardly been characterized at all. It has only been established that the butane fraction always predominates in the gaseous products. The liquid products have either not been investigated at all or have been characterized only as low molecular weight paraffinic hydrocarbons without indications as to their structure.

We studied the cracking of n-heptane, n-nonane, n-hexadecane and technical paraffin using the latest methods for investigating the reaction products.

EXPERIMENTAL

The study of the cracking reaction of n-heptane was carried out at temperatures of 50 and 98.5° with 10 and 20% $AlCl_3$, while that of nonane was carried out in the presence of 10% $AlCl_3$ at temperatures of 100 and 150°. The beginning of the formation of so-called "complex" compounds of the hydrocarbons and $AlCl_3$ (the lower dark colored layer) was accompanied in all cases by the cracking of the initial hydrocarbon with evolution of gas.

The characteristics of the initial individual hydrocarbons are set forth in Table 1.

TABLE 1
Characteristics of the Initial Hydrocarbons

Hydrocarbon	Boiling point (in °)		d_4^{20}		n_D^{20}	
	Our data	Literature data [19]	Our data	Literature data [19]	Our data	Literature data [19]
n-Heptane	98.5	98.4	0.6836	0.6839	1.3878	1.3877
n-Nonane	150.7	150.7	0.7177	0.7180	1.4060	1.4056

Sublimated aluminum chloride with the following characteristics: $AlCl_3$ 98.37%, $FeCl_3$ 0.05%, residue 1.58% was used in the study of the cracking of the hydrocarbons indicated above.

The experiments were carried out at atmospheric pressure in the presence of hydrogen chloride as an accelerator in the laboratory apparatus depicted in the figure. Hydrogen chloride was continuously supplied to the reaction zone.

The reaction products being formed, together with HCl were continuously conducted through a column with an electrical heating unit, 400 mm in height and 10 mm in diameter, joined to the reaction vessel. A ring of glass thread 0.5 mm in section served as packing for the column. The diameter of the ring was equal to 2-3 mm.



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The temperature regime of the fractionating column was established depending on the initial crackability of the hydrocarbon so that a minimal quantity of unreacted initial hydrocarbon, was eliminated from the reaction zone in the stream of gas which was being formed and hydrogen chloride which was introduced into the reaction. For example, during the cracking of n-heptane the temperature of the column was maintained at a level of 50-60° and during the cracking of n-nonane, 80-100°.

The gaseous cracking products were fractionated at low temperatures in a Podbielniak apparatus with subsequent analysis of the fractions obtained. The quantity of isobutane was determined in addition by the method of the critical temperature of solution of the butane fraction in o-nitrotoluene.

The liquid cracking products were subjected initially to stabilization and then to clear-cut rectification in a column with 40 theoretical plates under the operating conditions.

TABLE 2

Balance Sheet of the Cracking Products of n-Heptane and N-Nonane

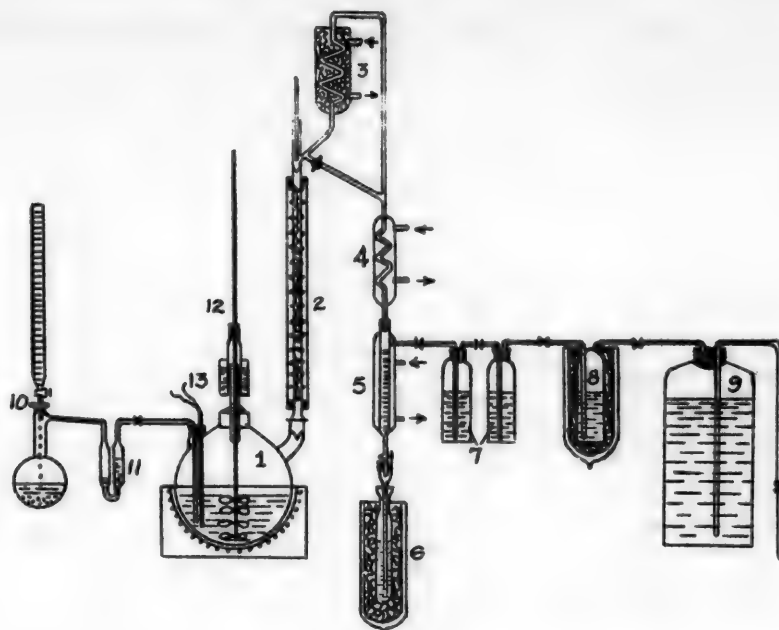
Experimental conditions	Yield, in weight % of the initial hydrocarbon			
	n-Heptane		n-Nonane	
Temperature (in °)	50°	98.5°	100°	150°
Weight percent of AlCl ₃	10	10	10	10
Total gas	19.8	24.0	19.8	21.0
Iso-C ₄ H ₁₀ included in the total gas	19.3	23.1	19.2	19.8
Boiling range of the fractions (in °):				
27-29.	8.3	9.3	10.5	11.5
29-38.	1.1	0.5	0.6	0.7
38-64.	6.7	4.7	4.2	5.7
64-77.	1.9	1.2	0.6	0.6
77-94.	8.9	2.3	1.3	1.5
94-100.	32.2	40.8	0.3 ¹⁾	0.6 ¹⁾
100-120.	3.0	—	1.0 ²⁾	0.8 ²⁾
120-140.	2.9	—	1.2 ³⁾	0.5 ³⁾
140-160.	2.3	—	39.6 ⁴⁾	39.5 ⁴⁾
Residue after rectification.	4.9	5.5	4.3	3.9
Hydrocarbons which are bound to AlCl ₃ and contained in the residue after cracking	8.0	11.7	16.6	13.7
Total percent of hydrocarbon conversion	67.7	59.2	60.4	60.5

Note: The fractions which boiled in the ranges: 1) 94-120°; 2) 120-140°; 3) 140-148°; 4) 148-150° consisted of unreacted n-nonane.

The physical constants (specific gravity, coefficient of refraction, critical temperature of solution in aniline) of the fractions obtained were determined to characterize them; for the fractions boiling below 100° the hydrocarbon composition was also determined by the Raman spectra method.

The balance sheet of the cracking products of n-heptane and n-nonane is set forth in Table 2, while in Tables 3 and 4 are presented the physical constants of the cracking products boiling below 100° and the characteristics of the cracking products boiling above 100°.

It follows from the data of Table 5 that increased reaction temperature during the cracking of n-heptane leads to an increased yield of gas (29.2% at a temperature of 50° and 40.5% at 98.5°, calculating on the basis of the n-heptane which had reacted); increase in the quantity of AlCl₃ only accelerates the reaction. Change in the temperature within the limits of 100-150° during the cracking of n-nonane has practically no influence on the total yield of gas, which amounts to 33-34% of the reacting hydrocarbon. The composition of the gaseous cracking products of n-heptane and n-nonane is very close. Isobutane appears to be the basic component of the gas. Unsaturated hydrocarbons are absent in the gas. Small quantities of methane, ethane, propane and an insignificant quantity of water appear as admixtures in the isobutane. The yield of propane is increased with increased cracking temperature. Thus, during the cracking of n-heptane, the yield of propane increases from 0.4% at 50° to 1.5% at its boiling point (98.5°), while during the cracking of n-nonane it increases from 2.3% at 100° to 5.2% at 150°.



Scheme of the laboratory apparatus for cracking hydrocarbons with AlCl_3 . 1) Reaction flask; 2) column with packing and electrical heating unit; 3) condenser; 4) cooler; 5) receptacle with cooler; 6) ampoule for benzene; 7) absorber for HCl; 8) trap for benzene; 9) gasometer; 10) apparatus for preparing HCl; 11) desiccator for HCl; 12) stirrer; 13) thermocouple.

The data of Table 2 show that the bulk of the liquid cracking products of n-heptane and n-nonane boil in the range 27-100°. The physical constants of the fractions boiling below 100° (Table 3) and their analysis by the Raman spectra method (Table 6) demonstrate that their basic components are isopentane, isohexanes and isoheptanes.

TABLE 3

Physical Constants of the Cracking Products of n-Heptane and n-Nonane Which Boil Below 100°

Hydrocarbon	Temp. of expt. (in °)	AlCl_3 (in weight %)	27-29° fraction		29-38° fraction	38-64° fraction		64-77° fraction		77-94° fraction	
			d_4^{20}	n_D^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}
n-Heptane	98.5	20	0.6197	1.3530	—	0.6538	1.3715	0.6675	1.3792	0.6816	1.3865
n-Heptane	50	10	0.6194	1.3536	1.3573	0.6534	1.3715	0.6678	1.3795	0.6814	1.3864
n-Heptane	98.5	10	0.6201	1.3540	1.3557	0.6522	1.3710	0.6674	1.3800	0.6818	1.3861
n-Nonane	100	10	0.6193	1.3530	1.3560	0.6534	1.3730	—	1.3780	0.6819	1.3870
n-Nonane	150	10	0.6196	1.3540	1.3563	0.6538	1.3728	—	1.3780	0.6816	1.3869

The yields of paraffinic hydrocarbons with an iso-structure (in percentages by weight) are calculated on the basis of reacted hydrocarbon in Table 7. As is evident from the data of Table 7, the yields of paraffinic hydrocarbons with an iso-structure formed as a result of the cracking of n-heptane at a temperature of 98° and the cracking of n-nonane at temperatures of 100 and 150° are arranged in diminishing order from isobutane to isoheptane. During the cracking of n-heptane at 50° the yield of the isoheptane fraction exceeds the yield of the isopentane and isohexane fractions. This is evidently to be explained by the favorable conditions (low temperature) for the isomerization reaction.

The basic cracking products of n-heptane and n-nonane appear to be isoparaffinic hydrocarbons with a methyl group at the second hydrocarbon atom (Table 6); along with isoparaffins with one methyl group in position

TABLE 4

Characteristics of the Cracking Products of n-Heptane and n-Nonane Boiling above 100° (in the Presence of a Quantity of AlCl₃ Equal to 10% by Weight)

Hydro-carbon	Temp. of expt. (in °)	Boiling range	d ₄ ²⁰		n _D ²⁰		Critical temp. of solution in aniline after sul-fonation	Percentage by weight of sulfonated hydrocarbons***
			prior to sul-fonation	after sul-fonation	prior to sul-fonation	after sul-fonation		
n-Heptane	50	100-120° fraction	0.6966	0.6968	1.3949	1.3949	74.6	0.0
n-Heptane	50	120-140° fraction	0.7138	—	1.4041	1.4035	76.4	2.4*
n-Heptane	50	140-160° fraction	0.7355	0.7349	1.4110	1.4108	78.6	0.0
n-Heptane	50	Residue after rectifica-tion, b.p. 160-298**	0.7741	0.7733	1.4320	1.4320	84.2	1.5
n-Heptane	98.5	Residue after rectifica-tion, b.p. 105-222**	0.7500	—	1.4230	—	73.5	2.2
n-Nonane	150	100-150° fraction	—	—	—	—	74.2	2.0
n-Nonane	150	Residue boiling above 150***, b.p. 148-250°	0.7659	—	1.4258	—	77.2	4.0
n-Nonane	100	Residue boiling above 150***, b.p. 152-253°	0.7662	—	1.4260	—	75.8	3.0

2 or 3, more highly branched isomers with two methyl groups in positions 2, 3, and 2,4 and also isomers with a quaternary carbon atom are formed. It should be noted that during the craking of n-heptane with the temperature of the experiment increased, the yield of the latter is considerably diminished.

TABLE 5

Composition and Yield of the Gaseous Cracking Products of n-Heptane and n-Nonane with AlCl₃ (in percentages by Weight)

Characteristic	n-Heptane			n-Nonane	
Temperature (in °)	50	98.5	98.5	150	100
Percentage by weight of AlCl ₃	10	10	20	10	10
Composition of the gas:****					
CH ₄	0.8	1.2	1.8	0.5	0.7
C ₂ H ₆	0.8	1.2	0.4	0.0	0.0
C ₃ H ₈	0.4	1.5	1.9	5.2	2.3
iso-C ₃ H ₁₀	97.5	96.1	95.9	94.3	97.0
n-C ₄ H ₁₀	0.5	0.0	0.0	0.0	0.0
Yield of gas:					
on the basis of the initial hydrocarbon	19.8	24.0	31.0	21.0	19.8
on the basis of the hydrocarbon which reacted	29.2	40.5	40.2	34.7	32.9

The quantity of products boiling above 100° which is formed during the cracking of n-heptane depends on the reaction temperature. Low experiment temperatures facilitate the formation of high boiling hydrocarbons while at higher temperatures their yield is diminished (Table 2).

This phenomenon can apparently be explained by the destructive alkylation reaction which takes place during the cracking of paraffinic hydrocarbons in the presence of AlCl₃ [9] and proceeds more appreciably under low temperature conditions.

* The specific dispersivity of the fraction was equal to 100.6

** The boiling range of the residues was determined by redistilling them from a Würtz flask 5 ml in capacity.

*** The sulfonation was carried out with three volumes of 98% H₂SO₄.

**** An insignificant quantity of hydrogen (0.01-0.02%) was contained in the gas.

TABLE 6

Individual Hydrocarbon Composition of the Fractions Formed During the Cracking of n-Heptane and n-Nonane with 10% AlCl_3 as Determined by the Raman Spectra Method*

Hydrocarbon composition (in % by weight)	Hydrocarbon, and temperature of the experiment						
	n-Heptane, 50°		n-Heptane, 98.5°		n-Heptane**	n-Nonane, 150°	
	Boiling range of the fractions (in °)						
	38-64	77-94	38-64	77-94	64-77	27-38	38-64
Isopentane.	—	—	—	—	—	100	—
2-Methylpentane	27	—	48	—	—	—	68
3-Methylpentane	45	—	20	—	18	—	20
2,2-Dimethylbutane	20	—	12	—	—	—	—
2,3-Dimethylbutane	8	—	10	—	—	—	—
n-Hexane	—	—	—	—	11	—	12
2-Methylhexane	—	35	—	40	—	—	—
2,4-Dimethylpentane.	—	35	—	18	50	—	—
2,3-Dimethylpentane.	—	—	—	16	—	—	—
2,2-Dimethylpentane.	—	—	—	—	8	—	—
2,2,3-Trimethylbutane.	—	30	—	26	12	—	—

TABLE 7

Yield of Isoparaffinic Hydrocarbons (in Percentages by Weight) Based on the Hydrocarbon Which Reacted (in the Presence of a Quantity of AlCl_3 Equal to 10% by Weight)

Hydrocarbon	Temperature (in °)	Isobutane	2-Methylbutane (isopentane)	Isohexanes	Isoheptanes
n-Heptane.	50	28.5	13.8	10.4	15.1
	98.5	39.0	16.5	8.3	5.3
n-Nonane.	100	31.9	18.4	6.3	2.8
	150	32.7	20.1	8.5	3.1

TABLE 8

Influence of Hydrogen Chloride on the Cracking of n-Heptane

Hydrocarbon	Yield in % by weight			
	In the presence of HCl		In the absence of HCl	
	Based on the initial n-heptane	Based on the n-heptane which reacted	Based on the initial n-heptane	Based on the n-heptane which reacted
Isobutane.	23.1	39.0	5.2	27.0
Isopentane.	9.8	16.5	2.5	13.2
Isohexanes.	4.9	8.3	2.4	12.7
Isoheptanes.	3.1	5.3	2.0	10.6
Hydrocarbons which are bound to AlCl_3 in the residue after cracking	11.7	19.8	1.8	9.1
Total percentage of conversion	59.2		19.4	

* The hydrocarbon composition of the fractions was determined in the molecular spectroscopy laboratory of the Moscow State University under the direction of V. M. Tatevsky.

** All the 64-77° fractions which were formed during the cracking of n-heptane in all the experiments were combined, since the physical constants of these fractions were very close.

Investigation of the high boiling cracking products of n-heptane and n-nonane showed that they basically consist of paraffinic hydrocarbons (Table 4).

The accelerating action of hydrogen chloride on the cracking reaction of n-heptane in the presence of AlCl_3 is shown in Table 8. It follows from the data of the table that the presence of HCl accelerates the cracking reaction by a factor of 3. The presence of HCl also influences the composition of the reaction products.

In the absence of HCl the yield of isobutane is considerably reduced, the yield of isopentane is somewhat lower, the yield of the isohexane fraction is increased by 4.5% and the yield of the isoheptane fraction is doubled (calculated on the basis of the hydrocarbon which reacted).

SUMMARY

1. The basic cracking products of n-heptane at 50 and 98.5° and n-nonane at 100 and 150° (which we have studied in detail for the first time) in the presence of 10% AlCl_3 and with the use of HCl as an accelerator are isobutane (32-39%), isopentane (14-20%), isohexanes (6-10%) and isoheptanes (3-5%).

2. Isomers with a methyl group at the second hydrocarbon atom are predominately formed, and in lesser quantity hydrocarbons with a methyl group in position 3, and more highly branched isomers with two methyl groups in positions 2,3, and 2,4 and isomers with a quaternary carbon atom. Paraffinic hydrocarbons with a normal structure are formed in insignificant quantities.

3. The gaseous cracking products basically consist of isobutane (94-97%) and contain insignificant quantities of methane (0.02-1.8%), ethane (up to 1.5%), propane (up to 5%) and hydrogen (hundredths of a percent).

4. Hydrocarbons boiling above 100° are formed in small quantities; according to their chemical structure they consist of paraffinic hydrocarbons.

5. The percent of conversion of n-heptane is increased by a factor of three by the use of hydrogen chloride as a cracking accelerator with other experimental conditions being kept equal. In the absence of HCl the yield of isobutane and isopentane is decreased and the yield of the isohexane and isoheptane fractions is increased.

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INVESTIGATIONS IN THE FIELD OF ALCOHOL OXIDES (OXIDOLS)

II. PREPARATION AND PROPERTIES OF α,β -ALCOHOL OXIDES OF THE ALIPHATIC SERIES

V. I. Pansevich-Kolyada and L. A. Kureichik

The properties of alcohol oxides in which the hydroxyl group is in the α,β - position to the oxide ring, have still hardly been studied at all.

N. A. Prilezhaev [1] in his classic investigations of α -oxides, cites three examples of alcohol oxides which he obtained by oxidizing allyl alcohol, geraniol and linalool with perbenzoic acid. The oxide of allyl alcohol, previously obtained by other routes [2], was readily hydrated in glycerin [3], while the hydration of geraniol and linalool dioxides proceeded only at the oxide ring, more distant from the hydroxyl group with the formation of glycerin oxides [4]. On this basis, N. A. Prilezhaev notes that the oxide ring of α,β -alcohol oxides is stabilized by the hydroxyl group while he referred the ready hydration of the oxide of allyl alcohol to the general rule that the first representative of a series differs from its homologs.

However, the oxides of methylstyrylcarbinol and ethylstyrylcarbinol obtained by T. E. Temnikova and V. A. Kropachev [5] by the hydrogenation of the oxides of benzalacetone and phenylpropionylethylene also readily underwent hydration with the formation of the corresponding substituted glycerins.

We obtained the α,β -alcohol oxide, 2-methyl-4-phenyloxido-2,3-pentanol- which has very interesting properties [6] by the oxidation of 2-methyl-4-phenylpenten-2-ol-4 by peroxyacetic acid. On heating in acidified water at room temperature in a desiccator over H_2SO_4 , P_2O_5 , $CaCl_2$ it, like certain pinacols [7] and benzalacetone oxide [4], is cleaved into acetophenone and isobutylene oxide. The latter is isomerized in the presence of acidic reagents, or by heating, into isobutyric aldehyde, the presence of which was established in the reaction products together with acetophenone. The cleavage of the alcohol oxide proceeds in air and in an alkaline medium, but considerably more slowly. In a semicarbazide solution it is always only acetophenone semicarbazone that is obtained, which indicates the absence of isomerization of the isobutylene oxide, which forms into isobutyraldehyde under these conditions.

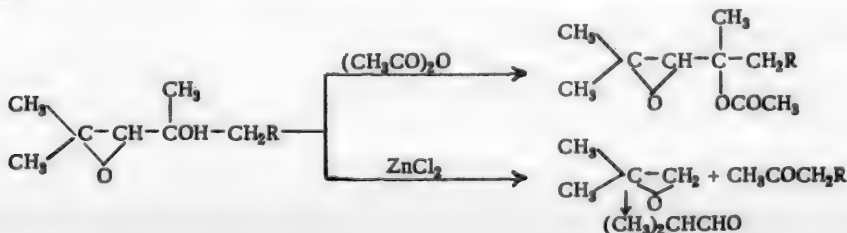
Thus, even these isolated examples of α,β -alcohol oxides show that the properties of these substances are far from being identical.

In the present work, we carried out the oxidation of 2,4,5-trimethylhexen-2-ol-4 and 2,4-dimethyldecen-2-ol-4 with peroxyacetic acid and studied certain properties of the α,β -alcohol oxides thereby obtained.

The oxidation of both alcohols was carried out with 80-92% peroxyacetic acid in absolute ether at a temperature of 20-25°. The reaction proceeded energetically and two α,β -alcohol oxides were obtained as a result - 2,4,5-trimethyloxido-2,3-hexanol-4 and 2,4-dimethyloxido-2,3-decanol-4.

They were rather mobile, colorless liquids with an odor reminiscent of the initial tertiary alcohols. Like the α -oxides they displaced iodine from a neutral potassium iodide solution. In other reactions, however, they markedly differed from the α -oxides of ethylenic hydrocarbons. The latter, as is well known [8], are acetylated at the oxide ring by the action of acetic acid and acetic anhydride, with the formation of mono- and diacetates of glycols, while the alcohol oxides obtained by us are acetylated at the alcoholic hydroxyl group with retention of the oxide ring when heated with acetic anhydride.

A still more marked difference is observed during the action of anhydrous zinc chloride on the alcohol oxides. Depending on the location of the oxide ring, α -oxides [9] are ordinarily isomerized by the action of this reagent into aldehydes or ketones. During the action of anhydrous zinc chloride on the α,β -alcohol oxides obtained by us the latter are cleaved like 2-methyl-4-phenyloxido-2,3-pentanol-4 [6] into isobutyraldehyde and the corresponding ketone:



The isobutyraldehyde and isobutyric ketones were determined by us as their derivatives with 2,4-dinitrophenylhydrazine, while isobutyraldehyde was also determined as its adduct with dimedone.

Cleavage proceeded most readily for 2,4,5-trimethyloxido-2,3-hexanol-4 which formed the hydrazones of isobutyraldehyde and methylisopropyl ketone even at ordinary temperatures in a hydrochloric acid aqueous solution of 2,4-dinitrophenylhydrazine.

Further study of these interesting compounds will show whether the cleavage of α,β -alcohol oxides under the action of zinc chloride which we have accomplished is a general property of these alcohol oxides, or whether this phenomenon is characteristic only of α,β -alcohol oxides of a specific structure.

We propose in the future, along with retention of the name alcohol oxides, to call these substances oxidols. The term oxidols, which can be extended to substances having several oxide rings or hydroxyl groups, more fully reflects the functional peculiarities of this series.

EXPERIMENTAL

I. Oxidation of 2,4,5-Trimethylhexen-2-ol-4 by Peroxyacetic Acid.

The alcohol was synthesized from isopropylmagnesium bromide and mesityl oxide:

b.p. 56-57° at 7 mm [10]; n_D^{20} 1.4500; d_4^{20} 0.8542; MR_D 44.67; calculated 43.08.

32.6 g of 92% peroxyacetic acid was slowly added to 55 g of the alcohol in 130 ml of absolute ether. The oxidation proceeded rather calmly; the temperature was kept equal to 20-25°. 2.79 g of unreacted peroxyacetic acid was left on the second day and this quantity hardly changed during 4 days, which indicated the end of the reaction. The acetic acid was neutralized with a soda solution and then with dry soda, and the ethereal layer was separated; the acidification products remaining were extracted with ether and the ethereal solution dried over $MgSO_4$. 46 g of substance with a b.p. of 69-70° was obtained by distillation at 8 mm. This was a readily mobile colorless liquid with a camphor odor. The alcohol oxide was readily oxidized with a 1% solution of permanganate, dissolved in cold water and organic solvents, and displaced iodine from potassium iodide. The semicarbazone was not obtained.

n_D^{20} 1.4340; d_4^{20} 0.9217; MR_D 44.64; calculated 44.34.

0.1586 g sub.: 0.3984 g CO_2 ; 0.1627 g H_2O . 0.2128 g sub.: 26.89 ml CH_4 (3°, 760 mm). 0.1124, 0.2126 g sub.: 19.4 g of benzene: Δt 0.191, 0.371°. Found %: C 68.51; H 11.74; OH 9.65; M 152.4, 151.8. $C_9H_{18}O_2$. Calculated %: C 68.29; H 11.47; OH 10.75; M 158.1.

A yellow-orange crystalline precipitate of the hydrazone was instantaneously formed with 2,4-dinitrophenylhydrazine. Two 2,4-dinitrophenylhydrazones were obtained by fractional crystallization from ethyl alcohol. The first fraction of hydrazone crystals melted at 170-172° and their analysis agreed with that of the 2,4-dinitrophenylhydrazone of isobutyraldehyde.

Found %: N 22.66; M 253.3. $C_{10}H_{12}O_4N_4$. Calculated %: N 22.22; M 252.

The discrepancy between the m.p. and the 2,4-dinitrophenylhydrazone of the isobutyraldehyde obtained by us and that indicated in the literature [11] should be noted.

The last fraction of 2,4-dinitrophenylhydrazone melted at 119-121° [11], and a mixed sample with a known preparation of methylisopropylketone displayed no melting point depression.

Reaction of 2,4,5-Trimethyloxido-2,3-hexanol-4 with Acetic Anhydride. 5 g of the alcohol oxide and 12 g of acetic anhydride were boiled for 12 hours, after which the reaction products were distilled at 9 mm. 1.2 g of substance with a b.p. of 109-112° (9 mm) was isolated. This was a colorless, mobile liquid with a geranium odor which rapidly dissolved in cold water and organic solvents, was readily oxidized by a one percent solution of permanganate, and displaced iodine from potassium iodide. The semicarbazone was not obtained. A test with methylmagnesium iodide demonstrated the absence of active hydrogen.

n_D^{20} 1.4437; d_4^{20} 0.9822; MR_D 54.1; calculated 53.52.

0.1803 g sub.: 0.4327 g CO_2 ; 0.1583 g H_2O . 0.1174 g sub.: 17.6 g of benzene: Δt 0.189°. Found %: C 65.45; H 9.82; M 189.9. $C_{11}H_{20}O_3$. Calculated %: C 66.0; H 10.0; M 200.

Reaction of 2,4,5-trimethyloxido-2,3-hexanol-4 with zinc chloride. 4 g of fused and pulverized $ZnCl_2$ was added to 15 g of the alcohol oxide. A slight evolution of heat and a strong turbidity was observed. During heating

on a water bath at 80-85°, the substance boiled and the liquid over ZnCl_2 became completely transparent. The heating was continued for 1.5-2 hours and the volatile products were collected in an alcoholic solution of dimedone. The latter was heated for 4 hours on a water bath; on the following day a crystalline product was obtained which melted at 150-151° [6] after recrystallization from alcohol. No melting point depression was observed in a mixed sample of it with the condensation product of dimedone with isobutyraldehyde.

The zinc chloride was dissolved in water, the reaction products were extracted with ether, dried over MgSO_4 , and after distilling off the ether were redistilled at ordinary pressure. 2.3 g of substance was isolated which boiled at 97-99° (740 mm). This was a colorless, mobile liquid with a pleasant odor, was readily soluble in organic solvents and in water, and rather rapidly decolorized one percent permanganate solution; active hydrogen was absent.

n_D^{20} 1.3935; d_4^{20} 0.8090; M_{RD} 25.4; calculated 25.3.

Found %: C 69.08; H 11.70; M 86.11. $\text{C}_6\text{H}_{10}\text{O}$. Calculated %: C 69.76; H 11.62; M 86.

A 2,4-dinitrophenylhydrazone was obtained which melted at 119° after recrystallization from ethanol.

II. Oxidation of 2,4-Dimethyldecen -2-ol-4 with Peroxyacetic Acid

The alcohol was synthesized from hexylmagnesium bromide and mesityl oxide.

B.p. 97° at 5 mm; n_D^{20} 1.4531; d_4^{20} 0.8378; M_{RD} 59.37; calculated 58.67.

0.1363, 0.1384 g sub.: 0.3945, 0.4001 g CO_2 ; 0.1603, 0.1624 g H_2O . Found %: C 78.90, 78.90; H 13.10, 13.20. $\text{C}_{12}\text{H}_{24}\text{O}$. Calculated %: C 78.20; H 13.04.

17 g of 80% peroxyacetic acid was gradually added to 33 g of alcohol in 66 ml of dry ether. The reaction proceeded energetically. The temperature of the reaction mixture was kept equal to 20-25°. All the peroxide had reacted after 4 days. The oxidation products were treated as in the preceding case. 15.5 g of substance with a b.p. of 123-124° was obtained by distillation at 6 mm. This was a colorless, rather mobile liquid, with odor resembling hexyl alcohol. The alcohol oxide was insoluble in water and dissolved in organic solvents; it decolorized KMnO_4 solution.

n_D^{20} 1.4412; d_4^{20} 0.9003; M_{RD} 58.60; calculated 58.01.

0.1268 g sub.: 0.3349 g CO_2 ; 0.1360 g H_2O ; 0.1942 g sub.: 20.05 ml CH_4 (0°, 760 mm). 0.0697, 0.1650 g sub.: 20.35 g of benzene: Δt 0.087, 0.193°. Found %: C 72.03; H 12.03; OH 7.88; M 202.4, 215.7. $\text{C}_{12}\text{H}_{24}\text{O}_2$. Calculated %: C 72.00; H 12.00; OH 8.50; M 200.

Reaction of 2,4-dimethyloxido-2,3-decanol-4 with zinc chloride. 0.4 g of fused ZnCl_2 was added to 2.0 g of the alcohol oxide. A marked turbidity of the entire liquid over the zinc chloride was at once observed, but when the liquid was heated on a water bath, as in the preceding case, it became completely transparent. The liquid, which had the odor of rancid fat, was poured off from the precipitate and distilled to 70° into an alcoholic solution of dimedone. Water was poured into the residue which had assumed an almost brown coloration, and a reddish layer thereupon separated which had a rather pleasant odor. A portion of this substance was added to a solution of 2,4-dinitrophenylhydrazine. Orange crystals rapidly settled out which melted at 58-59° after recrystallization from ethyl alcohol; this melting point agreed with that of the 2,4-dinitrophenylhydrazone of methylhexyl ketone [11]. The alcoholic solution of dimedone was heated for 2 hours on a water bath. Crystals precipitated on the next day which melted at 151° after recrystallization from ethanol. A mixed sample of these crystals with the condensation product of dimedone with isobutyraldehyde exhibited no melting point depression.

SUMMARY

1. Two unsaturated tertiary alcohols -2,4,5-trimethylhexen -2-ol-4 and 2,4-dimethyldecen -2-ol-4- were oxidized with peroxyacetic acid.
2. Two α,β -alcohol oxides -2,4,5-trimethyloxido-2,3-hexanol-4 and 2,4-dimethyloxido-2,3-decanol-4- were prepared.
3. During the action of acetic anhydride on 2,4,5-trimethyloxido-2,3-hexanol-4, acetylation proceeded at the alcohol group without change of the oxide ring.
4. Cleavage of the alcohol oxides into isobutyraldehyde and the corresponding ketones occurred during the action of anhydrous zinc chloride on the α,β -alcohol oxides obtained.

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THE SYNTHESIS OF CERTAIN β -HYDROXY ACIDS AND THEIR ESTERS

G. M. Borodina

The object of the present work was the synthesis of certain β -hydroxy acids and their esters; to wit: β -hydroxy tridecanoic, β -hydroxypentadecanoic and β -hydroxystearic (β -hydroxyoctadecanoic) acids.

In the literature there are directions only for the preparation of β -hydroxystearic acid along with α,β -octadecenoic acid during the heating of β -bromostearic acid with an alcoholic solution of potassium hydroxide [1]. However, both this reaction and the addition of water to unsaturated acids require the presence of the difficultly accessible α,β - and β,γ -unsaturated acids, and is accompanied by side reactions.

It is also well known that the mutual reaction of esters of halogen-substituted acetic acids with aldehydes in the presence of zinc powder (Reformatsky reaction) proceeds with satisfactory yields of esters of β -hydroxy acids only for aldehydes with a number of carbon atoms in the molecule that does not exceed 10-11 [2, 3].

Therefore, we accomplished the preparation of esters of β -hydroxytridecanoic, β -hydroxypentadecanoic and β -hydroxystearic acids via the reduction of the corresponding esters of β -ketoacids with the aid of aluminum amalgam in a medium of moist ether [4].

The initial β -ketoacid esters had not been described in the literature. There are only references to the preparation of the ethyl ester of β -ketotridecanoic acid from sodium acetoacetic ester and the acid chloride of undecanoic acid; however, this ester was not isolated and was only characterized in the form of the 1-phenyl-3-decyl-5-pyrazolone [5].

The esters of β -ketotridecanoic and β -ketopentadecanoic acids were obtained by us by partial acidolysis of the acylmalonic esters [6].

The ester of β -ketostearic (β -ketoctadecanoic) acid was prepared according to the method of Bowman and Fordham [7].

The acid chloride of palmitic acid was condensed with the monosodium derivative of the mixed benzylethyl ester of malonic acid, yielding the corresponding hexadecanoylmalonic ester. The latter was subjected to debenzoylation in the presence of palladinized barium carbonate (5% Pd) and the monoethyl ester of hexadecanoylmalonic acid thereby formed was decarboxylated at 80-100°.

The reduction of the esters of the β -keto acids was accomplished with the aid of aluminum amalgam in a moist ether medium.

The ester of β -hydroxyoctadecanoic acid was not subjected to purification, but was directly saponified to obtain β -hydroxyoctadecanoic acid.

β -Hydroxy acids of the general formulas $RCH(OH)CH_2COOH$, where $R = C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$ were obtained by saponification of the esters of β -hydroxytridecanoic, β -hydroxypentadecanoic and β -hydroxystearic acid with a water-alcohol solution of potassium hydroxide.

EXPERIMENTAL

Undecanoylmalonic Ester

A mixture of 59 g of malonic ester and 24 ml of anhydrous alcohol in 75 ml of anhydrous benzene was added to 9 g of degreased magnesium shavings which had been activated by heating with crystalline iodine, 27.5 ml of dry benzene and 2.5 ml of anhydrous alcohol. All the magnesium went over into solution in the course of 3-5 hours. 20.7 g of the acid chloride of undecanoyl acid (50%, calculating on the basis of the malonic ester) was added to the cooled solution of magnesiummethoxymalonic ester after the excess alcohol had been distilled off with the benzene (25-30 ml), and the mixture was heated and stirred for 1.5-2 hours. After decomposition with a 5% solution of sulfuric acid and elimination of benzene and malonic ester in a vacuum, the residue (42 g) consisted of raw undecanoylmalonic ester.

Ethyl Ester of β -Ketotridecanoic Acid

42 g of undecanoylmalonic ester was heated with a five-fold quantity of glacial acetic acid (38 g) and with 0.2 g of 98% sulfuric acid (0.22% of the weight of the reagents) for 3 hours on a water bath with a reflux condenser. After eliminating the sulfuric acid in the form of barium sulfate (1 g of barium carbonate was added), the excess acetic acid was distilled off in a vacuum. The residue was separated by vacuum distillation with a fractionating column. The first fraction with a b.p. of 120-145° at 20 mm consisted of methyldecylketone -10.3 g (44%); the second fraction with a b.p. of 128-135° at 1.5 mm -12.55 g (38.5%) appeared to be the ester of β -ketotridecanoic acid. After three-fold redistillation at 1.5 mm, the ester of β -ketotridecanoic acid had the form of a colorless, oily liquid, which gave a dark cherry color with ferrous chloride, b.p. 130-135° at 1.5 mm.

d_4^{20} 0.9254; n_D^{20} 1.4455; MR_D 73.7; calculated 73.15.

3.885 mg sub.: 10.041 mg CO_2 ; 3.590 mg H_2O . Found %: C 70.48; H 10.85, $C_{15}H_{28}O_3$. Calculated %: C 70.26; H 11.00.

Ethyl Ester of β -Hydroxytridecanoic Acid

15 g of the ester of β -ketotridecanoic acid in 300 ml of moist ether was reduced with 42 g of amalgamated aluminum shavings until a positive reaction with ferrous chloride was no longer observed (48 hours). Aluminum oxide was eliminated by filtration and washed and treated with hot alcohol. The solvent was distilled off from the combined filtrates. The residue was vacuum distilled. The ethyl ester of β -hydroxytridecanoic acid purified by a single vacuum redistillation had a b.p. of 166-169° at 10 mm; it was a colorless liquid with a fruity odor. The yield was 5 g (35%).

d_4^{20} 0.9234; n_D^{20} 1.4470; MR_D 74.71; calculated 74.65.

3.231 mg sub.: 8.27 mg CO_2 ; 3.332 mg H_2O . Found %: C 69.85; H 11.54, $C_{15}H_{30}O_3$. Calculated %: C 69.72; H 11.70.

β -Hydroxytridecanoic Acid

12 ml of a 40% solution of potassium hydroxide was added to 3 g of the ethyl ester of β -hydroxytridecanoic acid and the mixture was left for 12 hours at room temperature. The β -hydroxytridecanoic acid, obtained by acidification with dilute hydrochloric acid, had after threefold crystallization from petroleum ether, the form of colorless, light plates with a m.p. of 78-79°. The yield was 2 g (74.5%). The substance was soluble in alcohol, acetone and a solution of sodium bicarbonate.

3.646 mg sub.: 9.101 mg CO_2 ; 3.659 mg H_2O . Found %: C 68.12; H 11.22, $C_{13}H_{26}O_3$. Calculated %: C 67.77; H 11.37.

β -Hydroxypentadecanoic Acid

The tridecanoylmalonic ester was obtained in the same manner as the undecanoylmalonic ester by the reaction of the magnesiummethoxymalonic ester and the acid chloride of tridecanoic acid.

The ethyl ester of β -ketopentadecanoic acid was prepared according to the same method as the ethyl ester of β -ketotridecanoic acid - by the partial acidolysis of tridecanoylmalonic ester. After eliminating the acetic acid the residue was separated by fractional distillation at 0.5 mm. The first fraction with a b.p. of 60-120° and a weight of 8.5 g (37.6%) consisted of methyldecyl ketone; the 10 g (33.2%) of the second fraction boiled at 125-146°.

After threefold redistillation, the ethyl ester of β -ketopentadecanoic acid had the form of a viscous colorless liquid, which crystallized at a temperature below 20°, gave a sharp reaction for the presence of the keto group with ferrous chloride, and boiled at 137-142° at 0.5 mm.

d_4^{20} 0.923; n_D^{20} 1.4498; MR_D 82.74; calculated 82.32.

3.300 mg sub.: 8.672 mg CO_2 ; 3.327 mg H_2O . Found %: C 71.71; H 11.28, $C_{17}H_{32}O_3$. Calculated %: C 71.36; H 11.96.

The ethyl ester of β -hydroxypentadecanoic acid was prepared by reduction with aluminum amalgam in moist ether in the same manner as the ethyl ester of β -hydroxytridecanoic acid. It was a colorless, oily liquid with a b.p. of 155-159° at 1.3 mm.

3.631 mg sub.: 9.521 mg CO_2 ; 3.758 mg H_2O . Found %: C 71.55; H 11.58, $C_{17}H_{34}O_3$. Calculated %: C 71.26; H 11.96.

β -Hydroxypentadecanoic acid was prepared by saponifying the ethyl ester of β -hydroxypentadecanoic acid with a water-alcohol solution of potassium hydroxide in the same manner as β -hydroxytridecanoic acid. After three crystallizations from petroleum ether the substance had the form of thin white flakes with a m.p. of 76-77° that was soluble in alcohol, acetone and in sodium bicarbonate solution.

5.089 mg sub.: 12.981 mg CO₂; 5.364 mg H₂O. Found %: C 69.57; H 11.79. C₁₅H₃₀O₃. Calculated %: C 69.70; H 11.70.

Benzylethyl Ester of Hexadecanoylmaleonic Acid

48 g (0.2 mole) of the benzylethyl ester of maleonic acid [7] in 75 ml of dry benzene was added to 4.6 g of metallic sodium (0.2g-atom) under a layer of 200 ml of dry benzene while the mixture was being stirred. After the sodium had completely reacted, 30 g of the acid chloride of palmitic acid (0.1 mole) was added in drops to the thickening reaction mass, and it was heated for half an hour on a water bath with a reflux condenser. The precipitate which formed was separated on a Büchner funnel, washed with benzene and after having been suspended in ether was decomposed with a 10% acid solution. The ethereal solution was dried with sodium sulfate and the ether driven off. The residue (53 g) consisted of the crude benzylethyl ester of hexadecanoylmaleonic acid suitable for debenzylation and decarboxylation.

Ethyl Ester of β -Ketostearic Acid

30 g of the crude benzylethyl ester of hexadecanoylmaleonic acid in 200 ml of anhydrous alcohol was hydrogenated in the presence of 5 g of palladinized barium carbonate (5% Pd). The hydrogenation slowed down after 1070 ml of hydrogen had been absorbed. After 10 g of palladinized barium carbonate had been added in three stages, 240 ml more of hydrogen was absorbed; a total of 1310 ml was absorbed (the theoretical quantity was 1460 ml). The catalyst was separated by filtration and the filtrate was heated to boiling for about an hour. After completion of the decarboxylation and distilling off the alcohol in a vacuum, the residue was vacuum distilled at 1.5 mm. The yield of the 135-175° fraction, which gave a sharp reaction with ferrous chloride for the presence of the keto group, was 13 g (60%).

After threefold vacuum redistillation, the β -ketostearic acid ester had a b.p. of 162-172° at 1.5 mm, and solidified at a temperature below 15°.

3.799 mg sub.: 10.278 mg CO₂; 4.063 mg H₂O. Found %: C 73.83; H 11.97. C₂₀H₃₈O₃. Calculated %: C 73.57; H 11.73.

β -Hydroxystearic Acid

7 g of the ethyl ester of β -ketostearic acid was reduced in 200 ml of moist ether by 42 g of amalgamated aluminum shavings as in the preceding. The yield of the 144-147° (at 0.8 mm) fraction was around 3 g (43%).

3 g of the ethyl ester of β -hydroxystearic acid in 6 ml of alcohol was saponified with 12 ml of a 40% potassium hydroxide solution as in the preceding. The β -hydroxystearic acid had a m.p. of 86-87°. It consisted of thin white flakes (crystallized from petroleum ether). The yield was about 1 g.

2.278 mg sub.: 6.05 mg CO₂; 2.45 mg H₂O. Found %: C 72.47; H 12.03. C₁₈H₃₆O₃. Calculated %: C 71.93; H 12.08.

SUMMARY

1. The ethyl esters of β -ketotridecanoic and β -ketopentadecanoic acids were synthesized via the partial acidolysis of the acylmaleonic esters obtained by the reaction of magnesium methoxymaleonic ester with the acid chlorides of undecanoic and tridecanoic acids.
2. The ethyl ester of β -ketoctadecanoic acid was obtained by the debenzylation of the benzylethyl ester of hexadecanoylmaleonic acid in the presence of palladium on barium carbonate and by the decarboxylation of the monoethyl ester obtained.
3. The esters of the β -keto acids were converted into the esters of the corresponding β -hydroxy acids via reduction by aluminum amalgam in a medium of moist ether.
4. β -Hydroxy acids of the general formula RCH(OH)CH₂COOH, where R = C₁₈H₂₁, C₁₂H₂₅, C₁₅H₃₁ were obtained by saponification of their ethyl esters.

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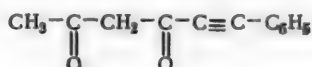
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CONDENSATION OF DIKETENE WITH CERTAIN ALIPHATIC KETONES

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There are no data in the literature concerning the synthesis of acetylenic β -diketones. Taking into consideration the great reactivity of diketene in addition reactions, we undertook the synthesis of the acetylenic β -diketone - 1-phenylhexene-1-dione-3,5



via the addition of phenylacetylene to diketene.

A number of our experiments in this field jointly with E. V. Kogan and K. A. Opaleva did not lead to positive results. In one of these experiments in which the reaction was carried out in acetone in the presence of pyridine, a liquid with a pleasant odor which gave characteristic reactions with ferrous chloride and bromine water, was obtained in place of the expected diketone. We assumed that this liquid consisted of the ester of acetoacetic acid and the enol form of acetone. We found no data in the literature concerning the reaction of diketene with ketones. On the contrary, in Boese's work [1], it was indicated that diketene does not react with ketones. However, this indication was found to be contrary to well-known data concerning the reaction of ketene (with which diketene is analogous in many of its properties) with ketones, with the formation of esters of acetic acid and the enol forms of the corresponding ketones [2].

On the strength of this the authors of the present work determined to investigate the reaction of diketene with certain aliphatic ketones - acetone, methylethyl ketone, and methylpropyl ketone - in greater detail.

Quite mobile, transparent, colorless liquids with a pleasant ethereal odor were obtained in all cases as a result of heating diketene with the indicated ketones in the presence of pyridine. The yield amounted to 50-55% of the theoretical, calculating on the basis of diketene. The constants of the substances obtained are given in the table.

TABLE

Formulas and designations of the substances obtained	B.p. (in °)	Pressure (in mm)	n_D^{20}	d_4^{20}	MR _D	
					Found	Calculated for the enol form
$\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}_2$ <p>α-Methylvinyl ester of acetoacetic acid (I)</p>	77	4	1.4678	1.0769	37.52	36.77
$\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_3$ <p>sym. Dimethylvinyl ester of acetoacetic acid (II)</p>	65	2	1.4696	1.0692	41.84	41.39
$\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_3$ <p>sym. Methyllethylvinyl ester of acetoacetic acid (III)</p>	71-72	2	1.4702	1.0533	47.50	46.01

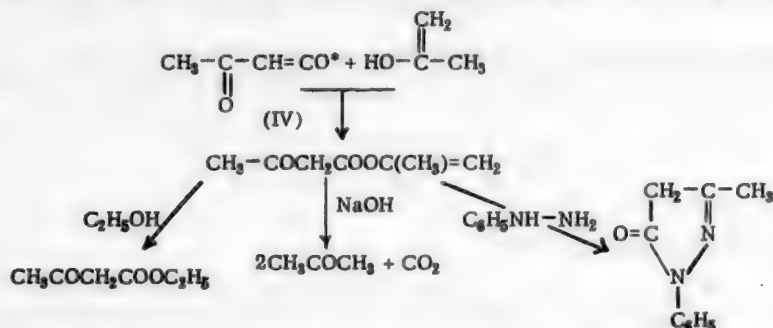
On the basis of the following facts we considered the products obtained to be ethers of acetic acid and enolic forms of the corresponding ketones formed by addition of the latter to diketene.

All the substances agreed in analytical data and molecular weight with the assumed empirical formulas (see substances (I), (II) and (III) in the table).

The ester (I) on heating with 5% alkali solution underwent saponification and ketone cleavage with evolution of approximately two moles of acetone per mole of ester.

On heating with absolute alcohol, the esters (I) and (II) underwent transesterification, forming acetoacetic ester with a 77% yield.

On heating with phenylhydrazine in the presence of absolute alcohol, (I) and (II) formed 1-phenyl-3-methyl-5-pyrazolone. The reaction of diketene (IV) with ketones proceeds according to the following scheme (for acetone):



The role of the catalyst —pyridine— in the condensation of diketene with ketones is evidently twofold. As a base it facilitates the enolization of ketones. On the other hand, pyridine, due to the presence of an incomplete electron pair at the nitrogen atom, activates diketene in the addition reaction (B. A. Porai-Koshits).

EXPERIMENTAL

The starting materials had the following characteristics:

diketene (98.5% pure) with a m.p. of 127.4° at 760 mm; 43° at 29 mm; d_4^{20} 1.0897; n_D^{20} 1.4379; **

acetone with a b.p. of 56-57°; d_4^{20} 0.792; n_D^{20} 1.3591;

methylethyl ketone with a b.p. 79-80°; d_4^{20} 0.805; n_D^{20} 1.3591;

methylpropyl ketone with a b.p. of 101-102°; d_4^{20} 0.810; n_D^{20} 1.3895.

The general procedure consisted of the following. A quantity of the ketone, usually five times as much volumetrically as the diketene, 0.5 ml of pyridine and 0.5 g of dry zinc sulfate were placed in a round-bottomed flask with a reflux water condenser. Diketene was slowly poured from a dropping funnel at room temperature. It was observed that some heat was evolved by the reaction mass and its temperature rose to approximately 28-30°, while the liquid became slightly yellow. The flask was shaken from time to time and then heated on a water bath for 4-6 hours. The conclusion of the reaction was determined by the disappearance of the diketene odor. The liquid became cherry red at the end of the reaction. The excess ketone was driven off in a column under a water jet pump and the residue was repeatedly fractionated under a vacuum at 2 or 4-5 mm.

I. Condensation of Diketene with Acetone

212 ml (3 moles) of acetone, 0.5 ml of pyridine, 0.5 g zinc sulfate and 39 ml (0.5 mole) of diketene were taken. After distilling off the acetone 53.6 g of substance was left which was redistilled under a vacuum at 3-4 mm. The chief fraction with a boiling point of 57-72° and amounting to 40 g (n_D^{22} 1.4635) after two repeated redistillations yielded 30.5 g of pure product with a b.p. of 77° at 4 mm, n_D^{20} 1.4678.

0.2522 g sub.: 0.5470 g CO₂; 0.1621 g H₂O. 0.1792 g sub.: 0.3846 g CO₂; 0.1124 g H₂O. Found %: C 59.19, 58.55; H 7.31, 7.02. C₇H₁₀O₅. Calculated %: C 59.15; H 7.09. 0.3944 g sub.: 30.26 g benzene; Δt 0.462°. Found: M 143.9. C₇H₁₀O₅. Calculated: M 142.

Hydrolysis and Cleavage. 4 ml of the ester with 1.5 ml of a 5% alkali solution was heated in a flask with a reflux condenser on a water bath for 6 hours. The contents of the flask were transferred to a flask with a fractionating column and 3.2 ml of acetone with a b.p. of 56-57° was distilled off. The yield was 73% of the theoretical.

* Four possible structural formulas are ascribed to diketene, including that set forth.

** The authors are grateful to B.A. Porai-Koshits and M.S. Dinaburg for kindly furnishing the diketene.

Transesterification. 14.4 g of the ester and 10.2 g of absolute alcohol were heated in a flask with a reflux condenser on a water bath for 10-12 hours. The liquid obtained was fractionated twice, first under a water jet pump and then in a vacuum at 14-15 mm. 8.9 g of a substance with a b.p. of 69-71°, n_D^{20} 1.4219 was collected. The product boiled at 180° at normal pressure. All of this agreed with the literature data for acetoacetic ester.

Preparation of 1-phenyl-3-methyl-5-pyrazolone. 5.4 g of phenylhydrazine (0.05 mole), 5 ml of absolute alcohol and 7.1 g (0.05 mole) of the substance were heated in a flask with a reflux water condenser and with a stirrer on a water bath for 6 hours. The reaction mass, poured into a glass and cooled, almost completely crystallized. The melting point of the raw product was 124° and was 126.5° for the recrystallized product. A mixed sample with pure phenylmethylpyrazolone yielded no depression. The yield of recrystallized product was 3.8 g.

II. Condensation of Diketene with Methyleneethyl ketone

50 ml of diketene, 175 ml of the ketone, 0.5 ml of pyridine and 0.5 g of zinc sulfate were taken.

After distilling off the excess ketone and repeated redistillation, 11.3 g of product with a b.p. of 65° at 2 mm, n_D^{20} 1.4696 was obtained.

0.1419 g sub.: 0.3176 g CO₂; 0.1049 g H₂O. 0.2123 g sub.: 0.4765 g CO₂; 0.1476 g H₂O. Found %: C 61.08, 61.25; H 8.27, 7.78. C₉H₁₂O₃. Calculated %: C 61.52; H 7.75. 0.4193 g sub.: 31.29 g benzene: Δt 0.429°. Found: M 159.3. C₉H₁₂O₃. Calculated: M 156.

Transesterification. 4 ml of the ester and 5 ml of absolute alcohol were taken. 2.3 g of a substance with a b.p. of 50-52° at 4 mm was obtained; n_D^{20} 1.4232.

Preparation of Phenylmethylpyrazolone. 3 ml of the ester, 2 ml of phenylhydrazine and 0.5 ml of absolute alcohol were taken. 0.8 g of a product with a m.p. of 126° was obtained. A mixed sample gave no melting point depression.

III. Condensation of Diketene with Methylpropyl Ketone

20 ml of diketene, 92 ml of the ketone, 0.5 ml of pyridine and 0.5 g of zinc sulfate were taken. 4.9 g of a product with a b.p. of 71-72° at 2 mm, n_D^{20} 1.4702 was obtained.

0.1597 g sub.: 0.3715 g CO₂; 0.1195 g H₂O. 0.1902 g sub.: 0.4411 g CO₂; 0.1433 g H₂O. Found %: C 63.42, 63.07; H 8.37, 8.43. C₉H₁₄O₃. Calculated %: C 63.52; H 8.29. 0.2592 g sub.: 32.19 g benzene: Δt 0.456°. Found: M 177.6. C₉H₁₄O₃. Calculated: M 170.2.

SUMMARY

1. The possibility of condensing diketene with aliphatic ketones — acetone, methylethyl ketone and methylpropyl ketone — was demonstrated.

2. It was demonstrated that the corresponding esters of the enol forms of the ketones and acetoacetic acid are formed at the same time, i.e., the *α*-methylvinyl, sym. dimethylvinyl and sym. methylethylvinyl esters.

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MONOVINYLACETYLENE HOMOLOGS

III. CYCLIC DIENE ETHERS

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As we have previously shown [1], during the reaction of a cyclic enyne hydrocarbon - 1-acetylenyl- Δ' -cyclopentene with methyl alcohol in the presence of borium fluoride and mercuric oxide, the simultaneous addition of one, two, or three molecules of alcohol to the hydrocarbon occurs.

In the present work most attention has been paid to the study of cyclic diene ethers of the general formula $C_nH_{2n-5}OR$, which had not previously been studied in any way.

Diene ethers were prepared for the first time by A. A. Petrov by the dehalogenation of the ethers of saturated and unsaturated hydrohalides [2, 3]. Particular interest attached to the synthesis of diene ethers derived from monovinylacetylene. A. E. Favorsky and his students showed in a number of examples that in the presence of KOH under pressure the formation of various substituted ethers proceeds and in particular the formation of β -substituted ethers [4, 5].

Klebansky and Chevychalova prepared acyloxy- and alkoxy derivatives of butadiene in the presence of mercuric oxide and boron fluoride [6, 7].

The introduction of an alkoxy group into the β -position of a diene system should increase its reactivity in the diene synthesis. Cyclic diene ethers, therefore, represent a suitable way to proceed via the diene synthesis on the one hand to various derivatives of bicyclic ketones of the decalone and hexahydroindanone series, and on the other hand, by reaction with quinone, to the little studied class of polycyclenediones and polycyclenettriones.

In discussing our results it is in the first place necessary to dwell on the synthesis of the initial cyclic enyne hydrocarbons. As was already indicated in the preceding article [1], the dehydration of acetylenic alcohols can be accompanied by a number of side reactions. 1-Acetylenyl- Δ' -cyclohexene was obtained by the dehydration of 1-acetylenylcyclohexanol-1 under various conditions.

In the last few years (1948-1952) indications have appeared in the literature to the effect that ethylbenzene [8, 9] is often contained in the dehydration products of 1-acetylenylcyclohexanol-1. However, no indications concerning the quantity of ethylbenzene as a function of the method of dehydration have been published.

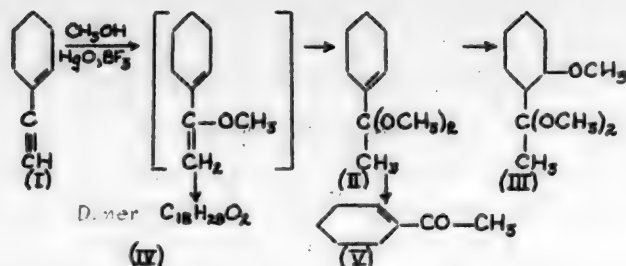
Our investigations showed that during catalytic dehydration over unfired porcelain and aluminum phosphate, the hydrocarbon obtained contains up to 80% in the first case and up to 20% in the second, of nonacetylenic hydrocarbon which did not add methyl alcohol in the presence of BF_3 and HgO (experiments 1-5, Table 1). The hydrocarbon recovered from the experiments did not yield a precipitate with an ammoniacal solution of cuprous oxide. It was established by spectroscopic investigation of it that it had the characteristic spectrum of ethylbenzene [10] (λ_{max} 2600 and 2650 Å). The isolated hydrocarbon was prepared by the action of phosphorus oxychloride in pyridine on carbinol [11].

We recorded analogous data previously during the dehydration of 1-acetylenylcyclopentanol-1. The isomerization of 1-acetylenyl- Δ' -cyclopentene in methylfulvene was presented in detail in the previous article [1]. In the present investigation, 1-acetylenyl- Δ' -cyclopentene was also prepared by the reaction of carbinol with phosphorus oxychloride in pyridine and did not contain methylfulvene.

The reaction of the hydrocarbons obtained with methyl alcohol in the presence of HgO and BF_3 was studied further and cyclic diene ethers were prepared.

The addition of methyl alcohol to 1-acetylenyl- Δ' -cyclohexene proceeded somewhat differently than to 1-acetylenyl- Δ' -cyclopentene (see the preceding article) with regard to the ratios of the reaction products obtained

The addition of methyl alcohol to 1-acetylenyl- Δ' -cyclohexene can be represented by the following scheme:

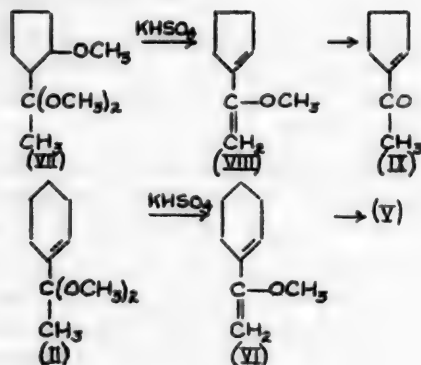


The following products were obtained as a result of the reaction: the dimethylketal of 1-acetyl- Δ' -cyclohexene (II) - 55%, the dimethylketal of 2-methoxy-1-acetylcyclohexene (III) - 3% and the dimer $\text{C}_{18}\text{H}_{28}\text{O}_2$ (IV) - 10%. The chief reaction product was the unsaturated ketal (II). The quantity of dimer was considerably less than in the case of the addition of alcohol to 1-acetylenyl- Δ' -cyclopentene. In view of the fact that the dimer (IV) and the methoxyketal (III) were obtained in insignificant quantities, they were not investigated in the present work.

The structure of product (II) was demonstrated by its hydrolysis in acid medium. The unsaturated ketone (V) was identified by comparison of its semicarbazone with the semicarbazone of 1-acetyl- Δ' -cyclohexene obtained by hydration of 1-acetylenyl- Δ' -cyclohexene.

Since 1-acetyl- Δ' -cyclohexene (V) was the standard for the demonstration of the structure of the unsaturated ketal and diene monoether of 1- α -methoxyvinyl- Δ' -cyclohexene (VI), the ultraviolet absorption curve of its semicarbazone was taken; the curve completely coincided with the absorption curve of the semicarbazone of the acetylcyclohexene obtained by the reaction of carbinol with formic acid [12, 20].

The cyclic diene ethers: 1- α -methoxyvinyl- Δ' -cyclohexene (VI) and 1- α -methoxyvinyl- Δ' -cyclopentene (VIII) were prepared by splitting off methyl alcohol from the corresponding ketals and methoxyketals by redistillation over small quantities of potassium bisulfate.

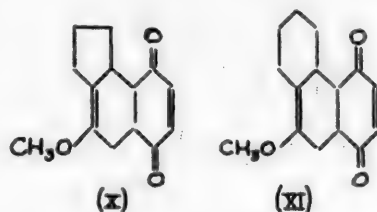


The structure of the diene ethers (VI) and (VIII) obtained was demonstrated by hydrolysis in the presence of dilute hydrochloric acid into the corresponding α,β -unsaturated ketones (V and IX).

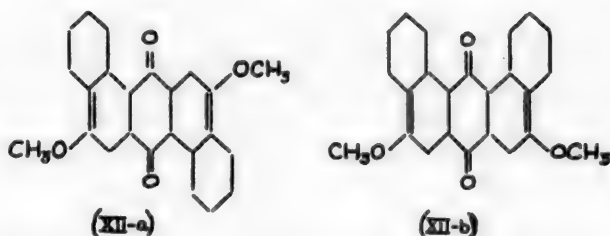
The unsaturated ketones were identified via comparison of their semicarbazones with the semicarbazones of 1-acetyl- Δ' -cyclopentene and 1-acetyl- Δ' -cyclohexene obtained by hydration by Kucherov's method of the corresponding enyne hydrocarbons.

The structure of the cyclic diene ethers obtained was also confirmed by diene condensation with quinones. During the addition of 1- α -methoxyvinyl- Δ' -cyclopentene to p-benzoquinone at room temperature even after a few minutes after the addition of the quinone, the formation of the addition product (1,2-cyclopentano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8) (X) was observed. The reaction was completed in the course of 1 hour. It was possible to stop the reaction at the stage of addition of one molecule of the diene to the dienophile only by quick addition of the quinone to the diene.

In the case of 1- α -methoxyvinyl- Δ' -cyclohexene, the formation of the addition product (1,2-cyclohexano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8) (XI) was observed only after several hours. To wholly complete the reaction it was necessary to leave the reaction mixture overnight.



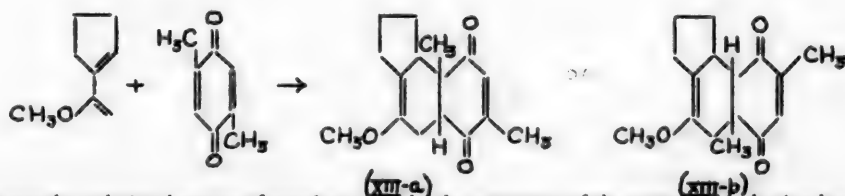
By the use of a large excess of the diene (VI) and slow addition of the quinone to the reaction mixture, it was possible to obtain as the unique reaction product the product of the addition of two molecules of the diene to quinone with a yield up to 30-50% (XII-a or XII-b):



The given case appears to be an almost unique example of the preparation of a double addition product at room temperature. The addition of two molecules of the diene to the quinone at room temperature was observed in addition to this example only for cyclopentadiene.

1-Vinyl- Δ' -cyclohexene forms a double addition product with quinone only upon boiling in tetralin with a yield of 10% [13]. By analogy with the double addition product of 1-vinyl- Δ' -cyclohexene, the addition product of two molecules of 1- α -methoxyvinyl- Δ' -cyclohexene (VI) to quinone probably has the formula (XII-a) (9,10-diketo-3,7-dimethoxyoctahydro-1,2,5,6-dibenzanthracene). It is evident on the basis of the facts set forth that 1- α -methoxyvinyl- Δ' -cyclohexene is more reactive in the diene synthesis than 1-vinyl- Δ' -cyclohexene.

The addition of 1- α -methoxyvinyl- Δ' -cyclohexene to p-xyloquinone led to the preparation of a tricyclic methoxydiketone with an angular methyl group



As regards a choice between formulas a and b, the structure of the compound obtained could not be determined in the present investigation.

With the object of demonstrating the structure of the compound (XIII) as a tricyclic α,β -unsaturated diketone with an angular methyl group, we took the ultraviolet spectrum of this compound (Fig. 1). These data coincided with the results obtained by Butz for a number of polycyclic diketone derivatives of 2-cyclohexene-1,4-dione [14].

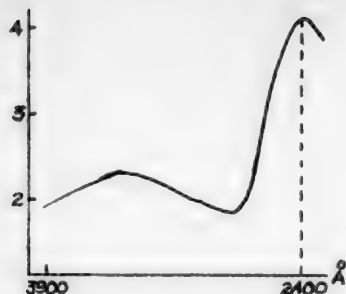
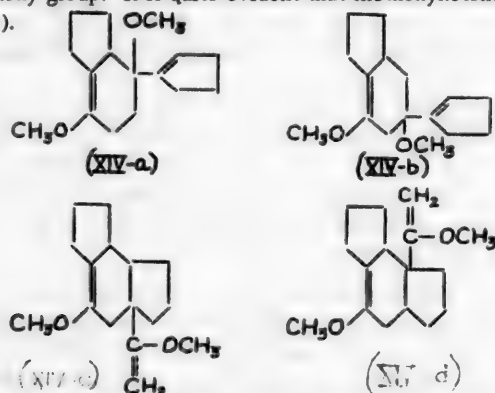


Fig. 1. Absorption curve of the tricyclic diketone with an angular methyl group. The solvent was ethyl alcohol; with 0.00002-0.00092 mole/liter $\lambda_{\text{max}} = 2400 \text{ Å}$ and $\epsilon = 10120$.

During the hydrolysis of the dimer with dilute hydrochloric acid the methoxy ketone $\text{C}_{15}\text{H}_{22}\text{O}_2$ was isolated, for which a semicarbazone was prepared which turned out to be a mixture of two isomeric semicarbazones. Both semicarbazones contained the methoxy group. It is quite evident that methoxyketones could be obtained only from the compounds (XIV-a) and XIV-b).



We tried to give another explanation of the formation of dimers of the diene ethers under the conditions of the addition reaction. It seemed more probable to us that dimerization proceeds in the instant of reaction under the influence of the catalyst BF_3 and HgO . With this object, analytically pure 1- α -methoxyvinyl- Δ' -cyclopentene was placed in contact with one drop of catalyst. A dimer analogous to the dimer (XIV) was obtained as a result. It is, consequently, quite evident that the dimer is formed not as a result of thermal dimerization, but as a result of the dimerization of the initially formed monoether under the influence of the catalyst. We consider that the yield of dimer during the addition reaction of alcohols to the vinylacetylenic hydrocarbons depends on the rates of two concurrent reactions — the rate of the dimerization reaction of the initially formed diene ether, and the rate of the addition reaction of a second alcohol molecule to the diene ether.

EXPERIMENTAL

1-Acetylenyl- Δ' -cyclohexene*

The initial 1-acetylenylcyclohexanol-1 was prepared according to Favorsky's method [16], by the condensation of cyclohexanone with acetylene in the presence of powdered potassium hydroxide. The yield of carbinol was 90%. B.p. 175-178°; m.p. 30-31° [17, 18].

* In the present article, we considered it more convenient to change the nomenclature of the compounds previously obtained, which were described in the preceding communication, and considered all the compounds as derivatives of cyclopentane and cyclohexane — for example, in place of Δ' -cyclopentenylacetylene — 1-acetylenyl- Δ' -cyclopentene; in place of 2,2-dimethoxy-2- Δ' -cyclopentenylethane — dimethylketal-1-acetyl- Δ' -cyclopentene.

Dehydration of 1-Acetylenylcyclohexanol-1

a) Over unfired porcelain. 45 g of the carbinol was passed in a stream of CO₂ through a glass tube filled with unfired porcelain. The temperature of the dehydration was 240-250°. The duration of the dehydration was 6 hours. The dehydration product was collected in a receiving flask, which was cooled with snow. The yield was 40%.

B.p. 47-49° at 20 mm; n_D^{16} 1.4970.

The hydrocarbon was a mobile, colorless liquid which yielded a characteristic precipitate with Ilosvay reagent and with an ammoniacal silver oxide solution.

b) Over aluminum phosphate. The catalyst was prepared by Ogloblin's method [19]. 20 g of aluminum phosphate obtained in this manner was stirred with 200 g of finely ground porous plates. Immediately before the dehydration, the catalyst was dried in a vacuum at 280-300°.

60 g of the carbinol was distilled for 3 hours in a nitrogen atmosphere through a glass tube filled with catalyst. The dehydration was carried out at 200 mm and 260-280°. The reaction product was collected in a receiving flask, cooled with a salt-snow mixture. The yield was 38.5%.

B.p. 76° at 100 mm; b.p. 47-49° at 20 mm; n_D^{16} 1.4975.

The hydrocarbon yielded a precipitate with an ammoniacal solution of silver oxide.

Preparation of 1-Acetylenyl- Δ' -cyclohexene

65 ml of phosphorus oxychloride in 65 ml of pyridine was added to 125 g of 1-acetylenylcyclohexanol-1 in 180 ml of pyridine at such a rate that the temperature was kept in a range of 105-110°. The reaction mass was energetically stirred. After the addition of all the phosphorus oxychloride the mixture was heated on a water bath for 1 hour, after which it was cooled to room temperature and poured out on ice. The pyridine was bound with 700 ml of 20% sulfuric acid and the hydrocarbon was extracted with ether. The ethereal solution was carefully washed with a solution of soda and dried with potash. The yield of hydrocarbon was 86%.

B.p. 74-75° at 90 mm; n_D^{20} 1.4956.

The hydrocarbon yielded the characteristic reactions for acetylenic hydrogen.

Addition of Methyl Alcohol to 1-Acetylenyl- Δ' -cyclohexene

The addition of methyl alcohol to 1-acetylenyl- Δ' -cyclohexene was carried out under the same conditions as the addition of methyl alcohol to 1-acetylenyl- Δ' -cyclopentene [1].

The conditions of the separate experiments and the yield of the products obtained are set forth in Table 1.

TABLE 1

Expt. No.	Quantity of reagents		Duration of the reaction (in hours)	Reaction temperature (in °)	Yield (in %)			Hydrocarbon recovered from the experiment (in g)
	hydro-carbon (in g)	alco-hol (in g)			of the dimethoxy derivative	of the trimethoxy derivative	of the dimer	
1	15	25	2	22-24	8	—	—	12
2	26	30	3.5	22-23	38	4.2	8	7
3	58	70	5.0	22-25	42.6	4	5.7	12
4	60	75	4.5	20-25	48.8	4.8	10	13
5	50	60	4.5	20-25	44.5	4.3	10.4	10
6	62	80	4.5	20-25	55.5	2.7	11	—

In the first experiment hydrocarbon was taken for the reaction which had been obtained by the dehydration of 1-acetylenylcyclohexanol-1 over unfired porcelain; in experiments 2-5, hydrocarbon obtained by dehydration over aluminum phosphate was taken; in experiment 6 — hydrocarbon obtained by dehydration with phosphorus oxychloride was taken.

The hydrocarbon recovered had constants close to those of the initial 1-acetylenyl- Δ' -cyclohexene. Spectroscopic investigation of it showed that it had the characteristic spectrum of ethylbenzene.

Investigation of the Addition Product of Two Molecules of Alcohol to 1-Acetylenyl- Δ' -cyclohexene

B.p. 91° at 17 mm; 56° at 2 mm; d_4^{20} 0.9712; d_4^{30} 0.9542; n_D^{20} 1.4618; MR_D 49.03; calculated 49.00.

0.1363 g sub.: 0.3563 g CO_2 ; 0.1348 g H_2O ; 0.0585 g sub.: 0.1514 g CO_2 ; 0.0577 g H_2O . 0.1849 g sub.: 17.0 g C_6H_6 ; Δt 33°. 0.1315 g sub.: 15.2 g C_6H_6 ; Δt 26°. 25.5 mg sub.: 17.7 ml 0.1 N $Na_2S_2O_3$. 25.4 mg sub.: 18.0 ml 0.1 N $Na_2S_2O_3$. Found %: C 70.73, 70.58; H 11.06, 11.06; M 170.73, 172.38; OCH_3 36.04, 36.61. $C_{19}H_{18}O_2$. Calculated %: C 70.54; H 10.66; M 170.24; OCH_3 36.46.

Hydrolysis of the Addition Product (II). 2 g of the substance (b.p. 55-56° at 2 mm and n_D^{20} 1.4617) was shaken in a test tube for several minutes with 6 ml of water and several (3-4) drops of hydrochloric acid. The hydrolysis product was salted out with potash and extracted with ether.

B.p. 89° at 18 mm; n_D^{16} 1.4907. The semicarbazone had a m.p. of 218-220°.

The data obtained corresponded with the literature data for 1-acetyl- Δ' -cyclohexene [12].

A mixed sample of the semicarbazone with a m.p. of 218-220° with the semicarbazone of known 1-acetyl- Δ' -cyclohexene displayed no melting point depression.

Preparation of 1-Acetyl- Δ' -cyclohexene. 0.3 g of mercuric sulfate and 45 ml of 70% aqueous methyl alcohol were placed in a flask supplied with a stirrer, a thermometer and a reflux condenser. The reaction mixture was energetically stirred and heated to 60° after which 9 g of 1-acetylenyl- Δ' -cyclohexene was added to it. The heating was continued for 2 hours in the course of which the temperature was held in the range 70-75°. Upon completion of the heating, the reaction product was cooled to room temperature and poured out into a mixture of an aqueous solution of salt and ether. The ethereal solution was dried with potash. The yield of ketone was 8 g.

B.p. 84° at 16 mm; d_4^{20} 0.9852; d_4^{30} 0.9692; n_D^{20} 1.4904; MR_D 37.0; calculated 36.28. The semicarbazone had a m.p. of 220-221° (from alcohol).

The ultraviolet absorption curve (Fig. 2) of the semicarbazone of 1-acetyl- Δ' -cyclohexene was taken.

Preparation of the Diene Ether - 1- α -Methoxyvinyl- Δ' -cyclohexene (VI)

The splitting off of methyl alcohol from the unsaturated ketal (II) was carried out via vacuum distillation at 120 mm over potassium bisulfate, which had been preliminarily heated to 200-202° and finely ground.

0.15 g of potassium bisulfate and around 10 g of the ketal (II) were placed in a flask with a branched fractionating column and two tubes and the reaction mixture was heated on Wood's metal to 130°; at this temperature, splitting off of the alcohol began. As soon as the temperature became constant, 10 g of the ketal was gradually added from a dropping funnel into the flask at the same rate as the diene monoether which was being formed distilled off. The reaction was carried out in a stream of dry nitrogen at 120 mm. After a single redistillation, a fraction was isolated which agreed in properties with the diene ether.

B.p. 44.5-45° at 1 mm; b.p. 123° at 95 mm; d_4^{20} 0.9638; d_4^{14} 0.9556; n_D^{14} 1.5095; MR_D 43.21; calculated 42.27.

0.0872 g sub.: 0.2479 g CO_2 ; 0.0787 g H_2O . 0.0909 g sub.: 0.2598 g CO_2 ; 0.0825 g H_2O . 26.5 mg sub.: 11.6 ml 0.1 N $Na_2S_2O_3$; 32.2 mg sub.: 14.7 ml 0.1 N $Na_2S_2O_3$. 0.1285 g sub.: 13.36 g C_6H_6 ; Δt 0.39°. 0.0835 g sub.: 19.55 g C_6H_6 ; Δt 0.16°. Found %: C 77.54, 77.94; H 10.09, 10.15; OCH_3 22.63, 22.44; M 138.1, 138.2. $C_9H_{14}O$. Calculated %: C 78.33; H 10.22; OCH_3 22.44; M 138.2.

Hydrolysis of the Diene Monoether (VI). 2.0 g of the substance was shaken in a test tube with 4 ml of 3% hydrochloric acid. The hydrolysis products were neutralized with potash and extracted with ether.

B.p. 85° at 14 mm, n_D^{17} 1.4900. The semicarbazone melted at 218°.

A mixed sample with known semicarbazone of 1-acetyl- Δ' -cyclohexene displayed no melting point depression.

Preparation of 1-Acetylenyl- Δ' -cyclopentene

The experiment was carried out under the conditions described above for 1-acetylenyl- Δ' -cyclohexene from 1-acetylenylcyclopentanol-1 with phosphorus oxychloride in pyridine. The yield of hydrocarbon was 75%.

B.p. 57-59° at 100 mm; n_D^{18} 1.4900.

The hydrocarbon was a colorless liquid with the characteristic odor of acetylenic hydrocarbons and gave a precipitate with an ammoniacal solution of silver oxide and Ilosvay's reagent.

Preparation of the Diene Monoether 1- α -Methoxyvinyl- Δ' -cyclopentene (VIII)

The splitting off of methyl alcohol from the methoxyketal (VII) was carried out by the method already described for the preparation of 1- α -methoxyvinyl- Δ' -cyclohexene (VI). It should be noted that it is not recommended that a large quantity of (VII) be taken for the cleavage reaction, since prolonged heating of the reaction products in the presence of potassium bisulfate can lead to dimer formation.

The diene ether (VII) was a transparent liquid, which rapidly was polymerized in air.

B.p. 78° at 35 mm; n_D^{20} 1.4942; d_4^{20} 0.9491; d_4^{20} 0.9316; MR_D 38.82; calculated 37.65.

0.0870 g sub.: 0.2448 g CO₂; 0.0744 g H₂O, 0.0910 g sub.: 0.2555 g CO₂; 0.0795 g H₂O. 25.00 mg sub.: 12.2 ml 0.1 N Na₂S₂O₃. 0.1717 g sub.: 21.15 g C₆H₆; Δt 0.33°; 0.1315 g sub.: 13.96 g C₆H₆; Δt 0.40°. Found %: C 76.57, 76.74; H 9.67, 9.77; OCH₃ 25.22; M 128.0, 124.2. Calculated %: C 77.40; H 9.65; OCH₃ 25.00; M 124.17.

The lowered percentage of carbon in the analyses of the diene ether should be noted. In spite of repeated redistillation, we did not succeed in isolating fractions with a higher index of refraction. As has already been indicated, the diene ether is very rapidly polymerized in air and apparently absorbs oxygen, which is probably responsible for some discrepancy in the analyses.

Hydrolysis of the Diene Ether (VIII). 3.5 g of the substance and 5 ml of 3% hydrochloric acid were shaken in a test tube for 15-20 minutes, whereupon an appreciable evolution of heat in the reaction mixture was observed. The reaction products were neutralized with soda, extracted with ether and dried with potash. 2.5 g of the ketone was obtained.

B.p. 55-56° at 8 mm; n_D^{16} 1.4815. The semicarbazone had a m.p. of 207-208° (from alcohol).

1-Acetyl- Δ' -cyclopentene (IX), obtained by the hydration of 1-acetylenyl- Δ' -cyclopentene had:

b.p. 61-61.5° at 12 mm; n_D^{16} 1.4824 [1].

A mixed sample of the semicarbazone of the hydrolysis product and the semicarbazone of the known ketone displayed no melting point depression.

The ultraviolet absorption curve of the semicarbazone of the ketone was taken (Fig. 3) [20].

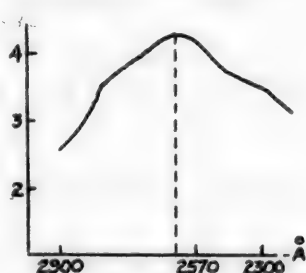


Fig. 2. Absorption curve of the semicarbazone of 1-acetyl- Δ' -cyclohexene. The solvent was ethyl alcohol; with 0.00113-0.00010 mole/liter, λ_{max} = 2570 Å, ϵ = 23 200.

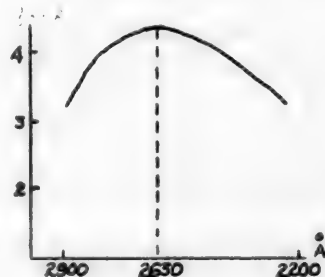


Fig. 3. Absorption curve of the semicarbazone of 1-acetyl- Δ' -cyclopentene. The solvent was ethyl alcohol; with 0.00305-0.00031 mole/liter, λ_{max} = 2630 Å, ϵ = 25 300.

Addition of 1- α -Methoxyvinyl- Δ' -cyclopentene to p-Benzoquinone

1 g of twice sublimed p-benzoquinone was added to 2.5 g of the diene ether (VIII) (n_D^{20} 1.4900) dissolved in 20 ml of methyl alcohol, in the course of 5 minutes while the mixture was energetically stirred (ratio of diene and dienophile 2:1). Evolution of the addition product began immediately after addition of the quinone. The reaction was completed in the course of 1 hour.

The bulk of the addition product (X) contained an insignificant admixture of double addition product. After two recrystallizations from a mixture of petroleum ether with benzene (5:1), the mono- addition product consisted of shiny, orange flakes with a m.p. of 102-103°.

9.6 mg sub.: 25.52 mg CO₂; 5.94 mg H₂O; 9.16 mg sub.: 24.42 mg CO₂; 5.86 mg H₂O. 22.8 mg sub.: 5.9 ml 0.1 N Na₂S₂O₃. 0.0830 g sub.: 16.81 g C₆H₆; Δt 0.11°. Found %: C 72.54, 72.75; H 6.92, 7.15; OCH₃ 13.41; M 232.5. Calculated %: C 72.41; H 6.89; OCH₃ 13.40; M 232.2.

Addition of 1-α-Methoxyvinyl-Δ'-cyclopentene to p-Xyloquinone

3 g of the diene ether in 30 ml of absolute benzene and 1 g of xyloquinone were heated in a sealed tube on a water bath for 14 hours. (The ratio of diene to dienophile was 3.3:1).

The mixture, which initially had a brown color, gradually acquired a bright yellow coloration. After eliminating the benzene in a vacuum, the residue entirely crystallized. The yield of the addition product (XIII) was 1.4 g (74%); the addition product recrystallized from petroleum ether consisted of shiny lemon-yellow flakes with a m.p. of 94°.

7.23 mg sub.: 19.65 mg CO₂; 4.89 mg H₂O. 7.93 mg sub.: 21.50 mg CO₂; 5.37 mg H₂O. 55.0 mg sub.: 12.7 ml 0.1 N Na₂S₂O₃. 48 mg sub.: 11.0 ml 0.1 N Na₂S₂O₃. 0.0985 g sub.: 15.41 g C₆H₆; Δt 0.13°. 0.1020 g sub.: 16.64 g C₆H₆; Δt 0.125°. Found %: C 74.12, 73.94; H 7.70, 7.57; OCH₃ 11.9, 11.9; M 254.6, 254.0. Calculated %: C 73.85; H 7.69; OCH₃ 11.9; M 260.32.

The ultraviolet absorption spectrum was taken for Compound (XIII) (see the theoretical part).

Addition of 1-α-Methoxyvinyl-Δ'-cyclohexene to p-Benzoquinone

Depending on the ratio of diene and quinone and on the rate of addition of the quinone to the diene ether in the reaction mixture, the ratio between mono- and double addition products is changed.

By slow addition of the quinone and a large excess of the diene ether, we succeeded in obtaining a double addition product as the only reaction product (experiment 3). On using benzene as the solvent, no double addition product at all was obtained (experiment 2).

TABLE 2

Expt. No.	Quantity of reagents (in g)		Ratio of diene to quinone	Solvent (in ml)	Duration of addition of the quinone (in minutes)	Duration of the reaction (in hours)	Yield (in %)	
	diene	quinone					of mono- addition product	of double addition product
1	3.5	1.5	2.3:1	CH ₃ OH (15)	120	14	27	28
2	1.4	0.3	4.6:1	C ₆ H ₆ (15)	15	14	73.5%	—
3	3.5	0.5	7:1	CH ₃ OH (20)	120	12	—	30

Mono- Addition Product (XI). After recrystallization from petroleum ether it consisted of yellow needles with a m.p. of 86-87°.

9.0 mg sub.: 24.05 mg CO₂; 6.14 mg H₂O. 7.72 mg sub.: 20.56 mg CO₂; 5.28 mg H₂O. 21.00 mg sub.: 5.1 ml 0.1 N Na₂S₂O₃. 0.0964 g sub.: 17.5 g C₆H₆; Δt 0.115°. 0.0810 g sub.: 15.5 g C₆H₆; Δt 0.12°. Found %: C 72.88, 72.63; H 7.63, 7.66; OCH₃ 12.47; M 248, 249.7. Calculated %: C 73.14; H 7.36; OCH₃ 12.6; M 246.

Double Addition Product (XII). After recrystallization from a mixture of benzene and petroleum ether (3:1) it consisted of fine white needles with a m.p. of 186°.

9.65 mg sub.: 26.4 mg CO₂; 7.32 mg H₂O; 4.81 mg sub.: 13.25 mg CO₂; 3.66 mg H₂O. 26.54 mg sub.: 8.09 ml 0.1 N Na₂S₂O₃. 0.0744 g sub.: 14.42 g C₆H₆; Δt 0.07°. Found %: C 74.66, 74.71; H 8.48, 8.48; OCH₃ 15.79; M 382. Calculated %: C 74.96; H 8.39; OCH₃ 16.14; M 384.4.

Dimerization of the Diene Monoether of 1-α-Methoxyvinyl-Δ'-cyclopentene Under the Influence of HgO and BF₃ · (C₂H₅)₂O

The catalyst was prepared in the same way as in the experiments involving the addition of methyl alcohol to hydrocarbon. 5 ml of anhydrous benzene and one drop of catalyst were placed in a reaction flask supplied with a

stirrer and a dropping funnel; 3 g of analytically pure monoether (n_D^{20} 1.4942, % OCH₃ 25.2) in a solution of 5 ml of anhydrous benzene was slowly added from a dropping funnel into the flask. The reaction mixture evolved heat vigorously and darkened. The reaction products were neutralized with finely ground potash (0.25 g), the residue filtered off, the benzene distilled off and the residue redistilled in a vacuum. 1.5 g of a substance with a b.p. of 145° at 2 mm was obtained which corresponded with the boiling point of the dimer C₁₆H₂₄O₂ (XIV).

The dimerization was carried out twice. 3.5 g of the dimer was obtained, which was then subjected to hydrolysis.

Hydrolysis. 3 g of the dimer was energetically shaken with 20 ml of 3% hydrochloric acid for 3 hours. The hydrolysis products were neutralized with soda, extracted with ether and dried with potash. 2.2 g of a ketone with a b.p. of 143-144° was obtained by distillation at 2.5 mm. The semicarbazone of the ketone was prepared which turned out to be a mixture of two isomeric semicarbazones. By fractional recrystallization from alcohol, the following were isolated:

1) a semicarbazone with a m.p. of 236-238°.

0.8020 g sub.: 10.45 ml N₂ (22°, 759 mm). 0.0560 g sub.: 7.2 ml N₂ (16°, 751 mm). 14.0 mg sub.: 2.75 ml 0.1 N Na₂S₂O₃. 23.8 mg sub.: 4.8 mg 0.1 N Na₂S₂O₃. Found %: N 14.82, 14.91; OCH₃ 10.15, 10.58. Calculated %: N 14.47; OCH₃ 10.65.

2) a semicarbazone with a m.p. of 220-222°.

0.0969 g sub.: 12.5 ml N₂ (20°, 758.6 mm). 0.1057 g sub.: 13.5 ml N₂ (24°, 764 mm). 22.8 mg sub.: 4.8 ml 0.1 N Na₂S₂O₃. 45.5 mg sub.: 9.4 ml 0.1 N Na₂S₂O₃. Found %: N 14.87, 14.60; OCH₃ 10.90, 10.70. Calculated %: N 14.47; OCH₃ 10.65.

Mixed samples with corresponding samples of semicarbazones obtained by hydrolysis of the dimer (XIV) displayed no melting point depression. Consequently, as a result of the hydrolysis of the dimer obtained during the low temperature dimerization of the diene ether 1- α -methoxyvinyl- Δ' -cyclopentene, a mixture of isomeric substituted hexahydroindanones is formed.

SUMMARY

1. It was shown that during the dehydration of 1-acetylenylcyclohexanol-1 over unfired porcelain and aluminum phosphate a hydrocarbon -1-acetylenyl- Δ' -cyclohexene- is formed which is isomerized into ethylbenzene.

2. The unsaturated dimethylketal 1-acetyl- Δ' -cyclohexene is formed as the chief reaction product by the action of methyl alcohol in the presence of BF₃·(C₂H₅)₂O and HgO on 1-acetylenyl- Δ' -cyclohexene.

3. The corresponding cyclic diene ethers: 1- α -methoxyvinyl- Δ' -cyclohexene and 1- α -methoxyvinyl- Δ' -cyclopentene were obtained by the cleavage of methyl alcohol from the dimethylketal of 1-acetyl- Δ' -cyclohexene and the dimethylketal of 2-methoxy-1-acetylcyclopentane.

4. The corresponding tricyclic methoxydiketones: 1,2-cyclopentano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8 and 1,2-cyclohexano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8 were obtained by the addition of 1- α -methoxyvinyl- Δ' -cyclopentene and 1- α -methoxyvinyl- Δ' -cyclohexene to p-benzoquinone.

5. The addition product of two molecules of diene to p-benzoquinone could be synthesized at room temperature by the use of an excess of the diene 1- α -methoxyvinyl- Δ' -cyclohexene.

6. A tricyclic methoxydiketone with an angular methyl group was obtained by the addition of 1- α -methoxyvinyl- Δ' -cyclopentene to p-xyloquinone.

7. The cyclic diene ethers obtained -1- α -methoxyvinyl- Δ' -cyclopentene and 1- α -methoxyvinyl- Δ' -cyclohexene- are reactive dienes and can be utilized for the synthesis of various polycyclic systems.

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CONDENSATION OF ANILINE WITH GLYCERIN, PARALDEHYDE AND ACETYLENE OVER ALUMINUM SILICATE

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It is mentioned in Chichibabin's communication [1] that lepidine, quinaldine and indole are formed by the passage over aluminum oxide of a mixture of acetylene and aniline vapors, with lepidine being formed in the largest quantity. Subsequently, Chichibabin and Oparina [2] carried out experiments involving the condensation of acetaldehyde and also of paraldehyde with aniline in the presence of aluminum oxide at 370-500°. The 220-270° fraction consisted of quinolinic bases and served for the preparation of the picrates of lepidine and quinaldine in a quantity of 28% of the first (experiments at 490-500°), and 6.5-10.4% of the second (experiments at 380-410°), calculating on the basis of the aniline which reacted. The authors expressed a hypothesis concerning the intermediate formation of crotonaldehyde, the presence of which they did not demonstrate experimentally [2].

The present investigation is devoted to elucidating the possibility of the direct synthesis of quinoline and also of quinaldine via the condensation of aniline with glycerin, paraldehyde and acetylene in the vapor phase over an aluminum silicate catalyst.

EXPERIMENTAL

The starting materials consisted of: 1) aniline with a b.p. of 183-184°; d_4^{20} 1.022, n_D^{20} 1.5863; 2) glycerin, dehydrated by heating to 180°; 3) paraldehyde with a b.p. of 124-125°, d_4^{20} 0.994; 4) acetylene, which was passed through a solution of potassium permanganate and chromic mixture before introduction into the reaction flask.

The experiments were conducted in an apparatus of the circulating type in a tube made of pyrex glass, in which aluminum silicate in the form of grains 2 mm in diameter was placed. A preliminary preheating was carried out in the upper part of the tube filled with glass rings. The aluminum silicate was replaced after each experiment. The fresh catalyst was activated by blowing air through it at 490-500° (4 hours). After each experiment, the catalyst was regenerated by blowing air at 500° for 2-3 hours through it until CO_2 was completely absent in the outgoing gas. The material balance of the experiments was arrived at according to the weight of raw materials and of the liquid and gaseous reaction products formed. The coke, resin and loss were calculated by differences.

Condensation of Glycerin with Aniline

In various experiments, glycerin was passed over aluminum silicate for 1 hour at 380° at a rate of 1 volume per 1 volume of catalyst per hour and for 20 minutes at 450° at a rate of 3 volumes per 1 volume of catalyst per hour. The liquid reaction products had a sharp odor and consisted of an aqueous and an oily layer. The water layer was separated and subjected to analysis. The test for the formation of a silver mirror was positive; dimedone gave a derivative which, after recrystallization from alcohol, melted at 191° (according to the literature data [3], the melting point of acrolein dimedone is 192°). Acrylic acid was produced by oxidation of the water layer with silver oxide. Found %: Ag 60.6, 60.3. Calculated %: Ag 60.1. The acrolein content, determined quantitatively by Ripper's method [5], turned out to be equal to 35.6% at 380° and 46.5% at 450°. The water content, determined by the carbide method [4], amounted respectively to 50 and 36%.

The gaseous reaction products chiefly consisted of hydrogen and carbon dioxide gas (see the table) which substantially differed from the gas obtained by Nef [6] by the pyrolysis of glycerin.

The yield (in percentage by weight) of acrolein at 380° amounted to 24% and at 450° to 26.2%, calculating on the basis of the glycerin passed through. Correspondingly, the yield of polymers was 7.9 and 12.3%, the yield of coke 19.3 and 20.2%, and the yield of water 33.9 and 20.3%. It is noteworthy that the portion of excess water in comparison with that which is formed by the dehydration of glycerin to acrolein amounts at 380° to 18.5% and at 450° to 3.5%. In view of the close yields of acrolein and coke and the twice greater yield of gas at 450°, it is necessary to assume that at 380° a considerable quantity of the acrolein which forms is converted into coke and polymers. At 450°, the basic sources for the formation of coke and polymers are the dehydration products of glycerin.

TABLE

Starting material	Experimental conditions			Gaseous reaction products (in volume %)				Yield of gas (in % by weight)
	Duration (in mins.)	Temp. (in °)	Volumetric rate	CO ₂	H ₂	C _n H _{2n}	C _n H _{2n+2}	
Glycerin	60	380	1:1	27.0	47.6	13.9	11.5	5.0
Glycerin	20	450	3:1	11.4	58.4	10.2	20.0	10.1
Glycerin + aniline	90	400	1:1	19.1	57.5	9.5	13.9	1.9
Aniline + paraldehyde	60	395	1:1	38.2	—	14.3	47.5	—
The same	60	400	1:1	43.4	—	16.2	40.4	—
Paraldehyde	30	370	1:1	41.0	—	50.0	9.0	12.6

After the experiments with glycerin, three experiments were carried out in which for an hour a mixture of aniline and glycerin (molar ratio 1:2) was passed over aluminum silicate at a temperature of 398-402° and a rate of 1 volume per 1 volume of catalyst per hour. The results of these experiments showed that on the average the yield (in % by weight) of aqueous layer amounted to 31.6%, of the oily products 49.9% and of coke 18.5%.

It was shown that increasing the duration of the experiment to an hour and a half did not change the results. In four experiments, a total of 150 g of the mixture was passed through and 122 g of liquid products was obtained.

The oily product (6.17 g) combined from the four experiments was rendered alkaline with sodium hydroxide and steam distilled. The base in the distillate separated in the form of an oily liquid; the aqueous part was extracted three times with ether. The oil was combined with the ethereal extract and the ethereal solution obtained was dried with solid alkali. The ether was distilled from the flask with a fractionating column, while the oily residue was distilled from a Würtz flask. The following fractions were taken off: 1st to 195°, 44.3 g (chiefly unreacted aniline); 2nd 195-210°, 1.23 g, n_D^{20} 1.5739, picrate m.p. 200.5°; 3rd 210-230°, 1.16 g, n_D^{20} 1.5071,

picrate m.p. 201.5°; 4th 230-244°, 9.70 g, n_D^{20} 1.6251, M 128, picrate m.p. 202.0°, iodomethylate m.p. 132.5°; 5th 244-250°, 2.25 g, n_D^{20} 1.6271, picrate m.p. 201.0°. There was 0.69 g of residue in the flask.

Calculating on the basis of the total fraction boiling above 195°, the yield of the fourth fraction amounted to 64.5%, which amounted to 19.2% calculating on the basis of the aniline passed through.

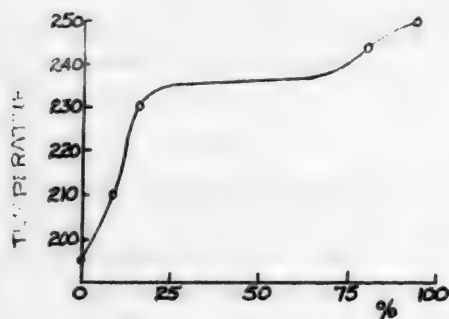
The character of the distillation curve indicates that the bulk of the 230-244° fraction boils at a temperature close to the boiling point of quinoline. The molecular weight and index of refraction of this fraction are close to those for quinoline; the melting points of the picrate and iodomethylate obtained from the 230-244° fraction corresponded with those for quinoline.

The literature data for quinoline: b.p. 238° [7], 239° [10], 237° [11, 12], n_D^{20} 1.6283 [13], picrate m.p. 203° [7, 10], iodomethylate m.p. 133° [10].

Condensation of Aniline with Paraldehyde

The conversion of paraldehyde over aluminum silicate was studied at 360-370° and a supply rate of 1 volume per 1 volume of catalyst per hour with an experimental duration of 25-35 minutes. The yield (average of three experiments in % by weight): 75.5% of liquid products, 12.8% of gaseous products, and 11.7% of coke (calculating on the basis of paraldehyde passed through). The quantity of unreacted acetaldehyde was 6.4%; the yield of the water-aldehyde portion of the catalyzate was 63.2% and the yield of oily product was 5.9%. The water-aldehyde portion of the catalyzate was subjected to fractional distillation into the following fractions: 1st 20-50°, 2nd 50-75°, 3rd 75-90°, 4th 90-103°.

The dimedone derivative of the 1st fraction melted at 140°, which was in excellent agreement with acetaldehydedimedone. The dimedone derivative prepared from the 4th fraction melted at 182°, which corresponded to the melting point of the corresponding crotonaldehyde derivative. The literature data for crotonaldehyde are [3, 10]: b.p. 103°, melting point of the dimedone derivative 183°. The content of H₂O in the aqueous layer, determined by the carbide method, was 15%.



Distillation curve.

Thus, paraldehyde, under the influence of aluminum silicate, is depolymerized into acetaldehyde, which then condenses in the crotonic pattern.

The gaseous products consist primarily of unsaturated hydrocarbons and carbon dioxide gas (see the table).

The experiments involving the condensation of aniline with paraldehyde were carried out at 380-400°, the volumetric rate was 1 volume per 1 volume of catalyst per hour; the duration of the experiment was 1 hour; the molar ratio of aniline to paraldehyde was 1:0.66. The yield (average of five experiments) of liquid products amounted to 86.0% by weight, calculating on the basis of the mixture passed through. The portion of the oily part in the products obtained amounted to 66.5%, of the water-aldehyde part 19.5%, and of coke 14%.

The oily portion of the catalyze was investigated by the method described above; it consisted of 74% of unreacted aniline and 26% of residue, which boiled above 195°. 7 g of nitrosocompound was obtained from 21 g of this residue, while the remaining portion was separated and fractionally distilled into the following fractions: 1st 195-210°, 2nd 210-223° and 3rd 223-250° (n_D^{20} 1.602, picrate m.p. 190°).

The yield of the 3rd fraction amounted to 14.8% by weight of the aniline passed through. The literature data for quinaldine [8, 10, 13]: b.p. 247°, n_D^{20} 1.607, picrate m.p. 191°.

The secondary amines obtained by reduction of the nitrosocompounds were fractionally distilled into the following fractions: 1st 195-200°, 2nd 200-214°, the 2nd fraction had n_D^{20} 1.5520; the picrate m.p. of 132°. The literature data [3, 10, 13] for ethylaniline: b.p. 204-205°, n_D^{20} 1.5559; picrate m.p. 132°.

Condensation of Aniline with Acetylene

In the condensation of aniline with acetylene the latter was introduced in a quantity approximately 2 times greater than that required according to the equation for the formation of quinaldine.

The experiments were carried out at 450°, the volumetric rate of aniline was 0.5 volumes per 1 volume of catalyst per hour and the duration of the experiment was 1 hour. The average yield of four experiments (in % by weight) of liquid products amounted to 95.8%, and of coke 4.2% of the aniline passed through.

The catalyze was analyzed as described above and yielded 26% of a residue which boiled above 195° and was further fractionally distilled into the following fractions: 1st 195-210°, 2nd 210-238°, 3rd 238-250°; the 3rd fraction had a n_D^{20} 1.602; picrate m.p. 187°. These values were close to those for quinaldine.

Another series of experiments was carried out at 450-460°; the volumetric rate of introduction of aniline was 0.4 volume per 1 volume of catalyst per hour; the acetylene was saturated with water vapor. The water was introduced into the reaction zone since the possibility of hydration of acetylene into acetaldehyde was assumed; further course of the reaction was according to the schemes described in the literature [9]. The yield (average of six experiments in % by weight) of liquid products amounted to 89% and 11% of coke based on the aniline passed through. The fractional distillation of the catalyze showed that it amounted to 61% of unchanged aniline and to 26% of a residue which boiled above 195°. After diazotization of this residue and separation of the nitrosocompound, the following fractions were obtained: 1st 195-210°, 1.7%; 2nd 210-232°, 2.4%; 3rd 232-250°, 5% (of the aniline passed through); the 3rd fraction had a n_D^{20} 1.604, the picrate m.p. 189.5°, the iodomethylate a m.p. of 194°. These data agreed with the literature data for quinaldine.

The composition of the outgoing gas: acetylene 24%, hydrogen 12%, saturated hydrocarbons 64%.

SUMMARY

1. The possibility of direct synthesis of quinoline, quinaldine and ethylaniline by the condensation of aniline with glycerin paraldehyde and acetylene in the vapor phase over aluminum silicate was demonstrated in principle. The catalytic action of aluminum silicate in this synthesis turned out to be analogous to the action of aluminum oxide observed by Chichibabin and Oparina.

2. It was established that under the influence of aluminum silicate glycerin is dehydrated to acrolein, the maximum yield of which, under the conditions studied, reaches 43 mole % of the glycerin taken.

3. It was shown that condensation of aniline with glycerin or paraldehyde proceeds under the influence of aluminum silicate with the evolution of hydrogen and with the formation of acrolein or crotonaldehyde as intermediate products. Consequently, the mechanism of the condensation which proceeds under the influence of aluminum silicate is analogous to the mechanism of the synthesis of Skraup and Dobner-Miller.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

VIII. CONDENSATION OF 2-METHYLCYCLOHEXANOL AND 3-METHYLCYCLOPENTANOL WITH BENZENE

N. G. Sidorova

Being occupied with the study of the condensations of cyclic alcohols with benzene in the presence of aluminum chloride, we set ourselves the goal of elucidating the degree and direction of isomerization of cyclic radicals as a function of the reaction conditions in the case of the isomeric methylcyclohexanols and methylcyclopentanols.

The condensations of methylcyclohexanols [1] and methylcyclohexenes [2] with aromatic compounds in the presence of acid catalysts are usually accompanied by isomerization with migration of hydrogen. As a result of the reaction of all the initial cyclic compounds substances are formed in which the aryl group is found at the same carbon atom to which the methyl group is attached. The condensation of analogous cyclopentane compounds (with the exception of 1-methylcyclopentanol and 1-chloro-1-methylcyclopentane [3]) has not been studied at all.

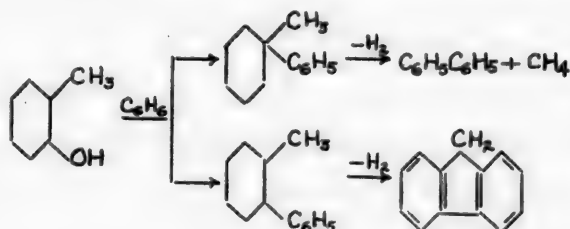
It seemed to us that the direction of the reaction in these condensations depends on the conditions and that under gentle conditions isomerization could be avoided. To verify this assumption, we studied the condensation of 2-methylcyclohexanol and 3-methylcyclopentanol with benzene under various conditions. In the case of 2-methylcyclohexanol, the isomerization should proceed particularly readily, since the methyl and hydroxyl groups are found on neighboring carbon atoms. The reaction with 2-methylcyclohexanol has already been studied by us together with Tsukervanik [4]. Under the conditions described, a product was obtained in a yield of 42.5% which, without special evidence, was taken to be 1-methyl-1-phenylcyclohexane.

The condensation of 1-chloro-2-methylcyclohexane with benzene in toluene in the presence of aluminum chloride has recently been described [5]. The author (also without evidence) ascribes the structure of 1-methyl-2-arylcylohexanes to the products obtained.

In pursuing the study of the condensation of 2-methylcyclohexanol with benzene, we were able to increase the yield of reaction product to 64% under conditions analogous to the previous. Investigation of the reaction product showed that it was almost wholly 1-methyl-1-phenylcyclohexane. The benzamino derivative obtained from it after three crystallizations had a m.p. of 235° and was shown to be identical with the benzamino derivative of a known sample of 1-methyl-1-phenylcyclohexane [6].

However, even in the earlier work [4], it was qualitatively noted that in this reaction a little hydrocarbon is formed, in which the phenyl group stands at the secondary carbon atom — evidently, 1-methyl-2-phenylcyclohexane. With the object of increasing the yield of this nonisomerized hydrocarbon, we carried out a number of condensations of 2-methylcyclohexanol with benzene under still more gentle conditions — during very slow addition of aluminum chloride and a very large excess of benzene (from 15 to 25 moles per 1 mole of alcohol).

The product obtained by the use of a 15-fold excess of benzene (yield 63% of the theoretical), was close in its constants to those of 1-methyl-1-phenylcyclohexane and the condensation product under severe conditions. The condensation product with the use of a 25-fold quantity of benzene (yield 73%) was appreciably different from them. Its dehydrogenation over platinum catalyst [7] yielded about 40% fluorene, approximately the same quantity of diphenyl, and some liquid hydrocarbon. The formation of these substances indicated that condensation under these conditions proceeds in two directions:



1-Methyl-2-phenylcyclohexane, evidently, is produced in the form of two stereoisomers.

Benzamino derivatives were obtained from the products of both the latter condensations which markedly differed from the benzamino derivatives of 1-methyl-1-phenylcyclohexane and the product of the first condensation, but they also differed among themselves. Both of these benzamino derivatives consisted of mixtures, and could not be entirely separated into the individual substances.

The condensations of 3-methylcyclopentanol with benzene were also carried out under various conditions. This reaction proceeds with considerably more difficulty than the analogous condensations of methylcyclohexanol and 1-methylcyclopentanol [3]. Only methylcyclopentene, chloromethylcyclopentane and the dimer of methylcyclopentene were formed with 0.7 g-equivalent of aluminum chloride. The reaction could be accomplished only with 0.9 g-equivalent of aluminum chloride and even in this case, a portion of the alcohol remained unreacted.

The condensation of 3-methylcyclopentanol with benzene both under gentle and under severe conditions yielded the same products - stereoisomeric 1-methyl-3-phenylcyclopentanes:



We did not succeed in even one case in demonstrating the presence of 1-methyl-1-phenylcyclopentane, although, possibly, it is formed in a large quantity.

The identification of the reaction products was achieved by the preparation of acetamino- and benzamino derivatives. Both of these derivatives were prepared in the form of mixtures. By fractional crystallization only one acetamino derivative and one benzamino derivative were isolated, evidently from the trans- form of the hydrocarbon.

Such a difference in the behavior of the methylcyclohexanols and methylcyclopentanol can be explained only by the fact that in the immobile five-membered ring, substituents are more rigidly bound.

EXPERIMENTAL

2-Methylcyclohexanol was prepared by the hydrogenation of o-cresol in the presence of Raney nickel at 180° and 120 atm. hydrogen pressure, measured at 20°. The b.p. was 164-166° (725 mm).

3-Methylcyclopentanol was prepared by the cyclization of β -methyladipic acid [8] and the hydrogenation of the ketone obtained over Raney nickel at 120° and 90 atm. hydrogen pressure, measured at 15°. The b.p. was 151-152°.

Condensation of 2-Methylcyclohexanol with Benzene Under Severe Conditions

In the reaction were taken: 2-methylcyclohexanol 11.4 g (0.1 mole), benzene 55 g (0.7 mole), AlCl_3 9.2 g (0.07 mole). Aluminum chloride was added to the mixture of methylcyclohexanol with benzene, during constant shaking of the reaction mixture, in small portions for 1 hour. The reaction mixture was then heated initially on a warm, and then on a boiling water bath to cessation of the evolution of the bulk of hydrogen chloride. The isolation of the reaction product was carried out in the usual manner. 11.12 g (63.8%) of a hydrocarbon with a b.p. of 225-250° was obtained. After two-fold distillation over sodium 1-methyl-1-phenylcyclohexane was isolated:

b.p. 119-121° (17 mm); d_4^{20} 0.9372; n_D^{20} 1.5210; M_R 56.58; calculated 56.43.

0.1002 g sub.: 0.3286 g CO_2 ; 0.0951 g H_2O . Found %: C 89.44; H 10.55. $\text{C}_{13}\text{H}_{18}$. Calculated %: C 89.65; H 10.35.

A benzamino derivative was obtained (by the usual method [9] without purification of the intermediate product) from the hydrocarbon, which had a m.p. of 223-230° prior to purification and even after three recrystallizations from alcohol melted at 235°.

5.05 mg sub.: 0.235 ml N_2 (725 mm, 25°). Found %: N 4.96. $\text{C}_{20}\text{H}_{23}\text{ON}$. Calculated %: N 4.78.

A mixture of it with the benzaminoderivative of 1-methyl-1-phenylcyclohexane (m.p. 235°) also melted at 235°.

Condensation of 2-Methylcyclohexanol with Benzene Under Mild Conditions

1. The following were taken in the reaction: 2-methylcyclohexanol 17.1 g (0.15 mole), benzene 175 g

(2.25 moles), AlCl_3 14 g (0.105 mole). Aluminum chloride was added to the water-cooled mixture of benzene and 2-methylcyclohexanol in very small portions for 6 hours while the mixture was energetically stirred.

Each successive portion was added only after complete solution of the preceding. The mixture was then left for 5 days (slight evolution of HCl occurred), after which several drops of water were added to it and the reaction was completed by heating on a warm water bath ($40-50^\circ$) for several hours to almost complete cessation of HCl evolution. The further treatment was as usual.

By distilling the reaction products 1.1 g of methylcyclohexyl chloride was obtained which redistilled at $90-100^\circ$ (95 mm) and 16.5 g (63.2%) of a mixture of hydrocarbons with a b.p. of $125-127^\circ$ (22 mm), which was purified by secondary distillation over sodium:

d_4^{20} 0.9355; n_D^{20} 1.5180; MR_D 56.41; calculated 56.43.

0.1045 g sub.: 0.3426 g CO_2 ; 0.0972 g H_2O . Found %: C 89.41; H 10.33. $\text{C}_{13}\text{H}_{18}$. Calculated %: C 89.65; H 10.35.

The benzamino derivative obtained from the alkylation product consisted of a mixture which was separated by fractional crystallization from alcohol and crystal sorting; two forms of crystals were thereby isolated - shiny needles and lusterless globules. The shiny crystals had a m.p. of $196-197^\circ$

5.16 mg sub.: 0.244 ml N_2 (29° , 723 mm). Found %: N 4.96. $\text{C}_{20}\text{H}_{25}\text{ON}$. Calculated %: N 4.78.

The lusterless crystals after isolation, melted at $170-175^\circ$. The results of their analysis agreed with those of the benzamino derivative of methylphenylcyclohexane.

7.85 mg sub.: 0.355 ml N_2 (19° , 722 mm). Found %: N 4.92. $\text{C}_{20}\text{H}_{25}\text{ON}$. Calculated %: N 4.78.

The melting point of this substance was increased by further crystallization and did not reach a definite limit. The crystal portion with the highest melting point melted at $196-202^\circ$.

II. The following were taken for the reaction: 2-methylcyclohexanol 15.6 g (0.137 mole), benzene 265 g (3.4 moles), AlCl_3 12.8 g (0.095 mole).

The reaction was carried out analogously to the preceding, but the mixture was left for 7 days. By distillation of the reaction products, 2.5 g of methylcyclohexyl chloride was obtained which redistilled at $95-100^\circ$ (100 mm) and 17.3 g (72.7%) of a mixture of hydrocarbons with a b.p. of $116-118^\circ$ (14 mm). Secondary distillation over sodium yielded the product:

B.p. $113-114^\circ$ (13 mm); d_4^{20} 0.9442; n_D^{20} 1.5249; MR_D 56.51; calculated 56.43.

Dehydrogenation [7]. A single passage of the hydrocarbons through a tube with platinized carbon at $300-320^\circ$ at a rate of 2-3 drops per minute yielded a catalyzate from which a liquid hydrocarbon with a b.p. of $124-126^\circ$ (15 mm); d_4^{20} 0.9979; n_D^{20} 1.5780, consisting of a mixture of unnamed hydrocarbons with the dehydrogenation product, was isolated by distillation. The residue after distillation was fluorene. The m.p. was 115° ; the picrate melted at 79° . The yield was around 10%. Repeated passage of the liquid hydrocarbon over catalyst at $320-340^\circ$ yielded a liquid catalyzate by distillation of which a fraction with a b.p. of $140-148^\circ$ (38 mm) was obtained which quickly crystallized. The crystals were shown to be diphenyl; m.p. 69° , yield around 40%. Fluorene (m.p. 115°) was in the residue after distilling off this fraction. The total yield of fluorene amounted to around 40%.

The benzamino derivative was isolated in the form of two modifications - lusterless crystals with a m.p. of $183-184^\circ$ and shiny needles which melted at $168-169^\circ$. Neither form consisted of a single substance.

Condensation of 3-Methylcyclopentanol with Benzene Under Mild Conditions

The following were taken for the reaction: 3-methylcyclopentanol 2.4 g (0.024 mole), benzene 53 g (0.68 mole), AlCl_3 2.8 g (0.021 mole). Aluminum chloride was added over a period of 1 hour. The mixture stood for 40 hours at room temperature and then was heated for 2 hours, initially on a warm water bath and then at 80° . The products were isolated in the usual manner. 2.15 g (56%) of 1-methyl-3-phenylcyclopentane was obtained:

B.p. $105-106^\circ$ (16 mm); d_4^{20} 0.9251; n_D^{20} 1.5142; MR_D 52.13; calculated 51.82.

Samples of 1-methyl-3-phenylcyclopentane are described in the literature as having the following constants: b.p. $230-235^\circ$; d_4^{17} 0.950; n_D^{17} 1.5276; b.p. $230-232^\circ$; d_4^{16} 0.937; n_D^{16} 1.5210; b.p. $93-94^\circ$ (12 mm); d_4^{17} 0.9173; n_D^{17} 1.5136 [10].

The acetamino derivative was prepared in the usual way. During its crystallization, flakes (chiefly) and lusterless globules precipitated from the diluted alcohol. During further purification of the flakes by crystallization from a mixture of benzene and petroleum ether, fine needle-like crystals with a m.p. of 150-151° were obtained.

6.34 mg sub.: 0.406 ml N₂ (26°, 726 mm). Found %: N 6.79. C₁₄H₁₉ON. Calculated %: N 6.49.

Benzamino derivative. Two sorts of crystals precipitated during crystallization from alcohol — transparent fine needles and lusterless globules (chiefly). It was not possible to separate them completely by mechanical means and, therefore, the entire mixture was further crystallized as a whole. After repeated crystallization, the melting point reached 188-189° (fine lusterless needles, grouped in globules).

11.98 mg sub.: 0.628 ml N₂ (26°, 726 mm). Found %: N 5.55. C₁₉H₂₁ON. Calculated %: N 5.02.

Condensation of 3-Methylcyclopentanol with Benzene Under Severe Conditions

The following were taken for the reaction: 3-methylcyclopentanol 7 g (0.07 mole), benzene 40 g (0.5 mole), AlCl₃ 8.7 g (0.065 mole). Aluminum chloride was added considerably faster than in the preceding case. The evolution of HCl and spontaneous heating of the reaction mixture were, thereupon, observed. Immediately after the addition of all the AlCl₃, the reaction mixture was heated on a water bath to the boiling point for 2 hours. 3.4 g (30%) of 1-methyl-4-phenylcyclopentane was obtained:

b.p. 114-116° (24 mm); d_4^{25} 0.9250; n_D^{25} 1.5120; M_R^D 51.95; calculated 51.82.

The acetamino derivative was purified analogously to the preceding. Flakes with a m.p. of 151° were obtained. A mixed sample with the acetamino derivative obtained from the product of the preceding condensation did not display melting point depression.

The benzamino derivative after repeated crystallization from alcohol had a m.p. of 187-189°.

SUMMARY

The condensations of 2-methylcyclohexanol and 3-methylcyclopentanol with benzene in the presence of aluminum chloride were studied under various conditions.

It was shown that in the case of 2-methylcyclohexanol, the reaction can proceed in two directions. Under mild conditions (large excess of benzene, slow addition of aluminum chloride, and low temperature) the condensation partially proceeds without isomerization of the alcohol radical; the reaction products are 1-methyl-2-phenylcyclohexane (apparently, a mixture of the cis and trans forms) and 1-methyl-1-phenylcyclohexane. Under more severe conditions, 1-methyl-1-phenylcyclohexane is formed almost exclusively.

The condensation of 3-methylcyclopentanol with benzene under analogous conditions is not accompanied by appreciable isomerization of the alcohol radical.

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• See Consultants Bureau Translation, page 1463.
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PHOTOREACTIONS OF METALLOORGANIC COMPOUNDS OF MERCURY IN SOLUTIONS

XIV. PHOTOREACTIONS OF β -MERCURIBISPROPIONIC ACID AND ITS DIMETHYL ESTER

G. A. Razuvaev, Yu. A. Oldekop and V. N. Latyaeva

In a number of preceding works, we have investigated the photoreactions of Ar_2Hg and Alk_2Hg in solutions, which proceed via the formation of free radicals. The radicals which are formed react both with the solvent and with each other, depending on their nature. The photodecomposition of diethylmercury and diphenethylmercury [1] proceeds with the disproportionation of the ethyl radicals into ethane and ethylene, or of phenethyl radicals into styrene and ethylbenzene, keeping pace with the splitting off of hydrogen radicals from the solvent — the basic reaction for methyl and phenyl radicals. In addition to these reactions, the dimerization of radicals should be noted, as it occurs for the benzyl radical [2]. It seemed to us of interest to investigate the influence of functional groups on the reactivity of the radical. We selected β -mercuribispropionic acid and its dimethyl ester as an example. This compound, obtained for the first time by Fischer [3], is completely nontoxic and, therefore, has found application in medicine [4]. However, the chemical properties of this acid have hardly been sufficiently described.

β -Mercuribispropionic acid was prepared by us by Fischer's method, starting from the methyl ester of β -iodopropionic acid and 0.5% sodium amalgam. The dimethyl ester of β -mercuribispropionic acid was isolated for the first time in the pure form.

The photoreaction of β -mercuribispropionic acid was investigated in solutions of methanol and the monoethyl ether of ethyleneglycol. The photoreaction proceeded with the evolution of mercury and the formation of propionic and adipic acids. The propionic acid was obtained due to the dehydrogenation by the β -carboxyethyl radical of the solvent alcohol with the formation of formaldehyde or of acetaldehyde. The disproportionation reaction of the radicals which should yield propionic and acrylic acids, was not observed by us. The reaction involving the splitting off of hydrogen prevailed. The course of the reaction can be represented by the following scheme:



(chief reaction $\sim \frac{2}{3}$)



(side reaction $\sim \frac{1}{3}$)

The photoreaction with the dimethyl ester of β -mercuribispropionic acid proceeds analogously. The presence of a gradual splitting off of radicals (reactions 1 and 2) is indicated by the photoreaction of this ester in chloroform, during which β -carbomethoxyethylmercury chloride and the methyl ester of propionic acid were isolated; the radicals formed according to equation (1) react with chloroform with the removal of chlorine (5) and hydrogen (6):



In addition, mercury (in accord with equation 2) and calomel, formed due to the chlorinating action of chloroform on mercury during the irradiation were found.

The ester of adipic acid was not found in the reaction products. Thus, in this case only the splitting off of the hydrogen of the β -carbomethoxyethyl radicals occurs.

This kind of reaction is impossible in benzene solution. And, actually, during the irradiation of the dimethyl ester of β -mercuribispropionic acid in benzene, mercury and the dimethyl ester of adipic acid were isolated. Thus,

reactions (1), (2) and (4) occurred. It is of interest to note that by the introduction of a carboxyl group into the ethyl radical, the disproportionation reaction is entirely suppressed, which has great significance in the photoreactions of diethylmercury and diphenethylmercury.

EXPERIMENTAL

The reaction was carried out in thin quartz test tubes with an internal diameter of 18 mm; the illumination was produced by a mercury-quartz lamp (Original Hanau, Hohen Sonne).

Photoreaction of β -mercuribispropionic acid in methanol. 3.0 g of β -mercuribispropionic acid in 20 ml of methanol was illuminated for 100 hours. In the reaction period 1.13 g of metallic mercury, or 97.6% of the theoretical quantity, was isolated. The mercury was filtered off (the filtrate did not decolorize bromine water); the filtrate was subjected to redistillation on a water bath and the distillate gave the silver mirror reaction. In addition, the dimedone formaldehyde derivative was obtained with a m.p. of 187°. Water was added to the residue after distilling off the methyl alcohol, and adipic acid, thereupon, precipitated. After recrystallizing it from ethyl acetate, it had a m.p. of 144°. A mixed sample with adipic acid displayed no melting point depression.

The weight of the adipic acid obtained was 0.2 g, or 23.8% of the theoretical. The aqueous solution obtained after isolating the adipic acid had an acid reaction (decolorization of bromine water was not observed); it was back titrated. 61.2 ml of 0.1 N KOH was consumed in the titration, which corresponded to 0.45 g of propionic acid, or 52.4% of the theoretical quantity.

Analysis of the silver salt:

0.3086 g sub.: 0.1825 g Ag. Found % Ag 59.14. $C_3H_5O_2Ag$. Calculated % Ag 59.66.

Photoreaction of β -mercuribispropionic acid in the monoethyl ether of ethylene glycol. 5.0 g of β -mercuribispropionic acid in 25 ml of the monoethyl ether of ethylene glycol was irradiated for 100 hours. 2.85 g of mercury was isolated after this period, which amounted to 98.3% of the theoretical quantity. The filtrate obtained after isolation of the mercury showed an aldehyde reaction (silver mirror). The dimedone acetaldehyde derivative was also isolated with a m.p. of 135°. The filtrate was diluted with water; a precipitate of adipic acid thereupon fell out, which, after recrystallization from ethyl acetate, had a m.p. of 144°. There was no melting point depression of this substance mixed with adipic acid. The weight of the acid obtained was 0.56 g, or 26.4% of the theoretical quantity.

Propionic acid was determined in the aqueous solution. 210.0 ml of 0.1 N KOH was consumed in the titration, which corresponded to 1.55 g of propionic acid, or 72.9% of the theoretical quantity. To identify the propionic acid, its p-bromophenacyl derivative was prepared and had a m.p. of 61°. A mixed sample of this substance with the derivative obtained from known propionic acid exhibited no melting point depression. A test for an unsaturated compound (bromine water) gave a negative result.

Photoreaction of the dimethyl ester of β -mercuribispropionic acid in chloroform. 5.0 g of the dimethyl ester in 25 ml of chloroform was irradiated for 24 hours. After this period, 0.92 g of metallic mercury and 0.2 g of calomel were isolated, which corresponded to 31.8% and 6% of the theoretical quantity, respectively. The mercury and calomel were filtered off. The filtrate was subjected to fractional distillation from a Würtz flask, and the 60-82° range fraction was collected. The residue after distilling off the solvent was subjected to steam distillation. The distillate consisted of the dimethyl ester of β -mercuribispropionic acid and had the characteristic camphor odor due to the presence of a small quantity of hexachloroethane.

The residue from the steam distillation consisted of a yellowish liquid from which β -carbomethoxyethylmercury chloride crystallized out on standing. It was filtered off and had a melting point of 60° (from acetone). There was no melting point depression of this substance with specially prepared β -carbomethoxyethylmercury chloride. 1.0 g of β -carbomethoxyethylmercury chloride or 22.5% of the theoretical was obtained. The filtrate after isolation of the β -carbomethoxyethylmercury chloride consisted of unreacted dimethyl ester of β -mercuribispropionic acid, and together with the distillate from the steam distillation, amounted to 1.9 g, or 38% of the initial quantity. 0.3 g of the methyl ester of propionic acid with a b.p. of 79-81° could be isolated from the fraction which boiled in the 60-82° range in an effective column. The benzylamino derivative of this ester was prepared for identification and melted at 43°, which corresponded with the literature data.

Photoreaction of the dimethyl ester of β -mercuribispropionic acid in benzene. 5.0 g of the dimethyl ester of β -mercuribispropionic acid in 25 ml of benzene was irradiated for 300 hours. The metallic mercury -2.63 g (quantitative yield)- was filtered off. After distilling off the benzene from the filtrate 2.13 g of the ester of adipic

acid was left and was saponified. Adipic acid was isolated in a yield of 90% with a m.p. of 149° after recrystallization from ethyl acetate. There was no melting point depression with known adipic acid.

SUMMARY

1. Quantitative evolution of mercury occurs during the irradiation with ultraviolet light of solutions of β -mercuribispropionic acid in methanol or in the monoethyl ether of ethylene glycol. Due to the splitting off of hydrogen from the solvent, the carboxyethyl radicals form propionic acid and, as a result of the dimerization of these radicals, adipic acid is formed. Aldehydes were detected in both cases.

2. The formation of β -carbomethoxyethylmercury chloride and the methyl ester of propionic acid occurs during the photoreaction of the dimethyl ester of β -mercuribispropionic acid in chloroform. Mercury and calomel were also detected.

3. Only adipic acid and mercury were found upon the photoreaction of the dimethyl ester of β -mercuribispropionic acid in benzene.

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* See Consultants Bureau Translation, page 1489.



REACTION OF ACYL PEROXIDES WITH METALS AND METAL CHLORIDES

(TIN AND ANTIMONY)

G. A. Razuvaev, B. N. Moryganov, E. P. Dlin and Yu. A. Oldekop

The decomposition of perbenzoic acid in solutions is ordinarily represented as involving the evolution of CO_2 and the formation of two radicals C_6H_5 and $\text{C}_6\text{H}_5\text{COO}$. However, on the basis of more detailed study it can be considered that the evolution of CO_2 is a secondary process; initially dissociation of the O—O bond occurs and then the benzoate radical loses CO_2 . There are a number of works in which the reaction of peroxides proceeding without evolution of CO_2 is described. Thus, the reaction of perbenzoic acid in alcohol or in benzene and in their mixtures in the presence of hydroquinone [1], with triphenylbismuth [2] and with metallic mercury in benzene solution [3] all proceed.

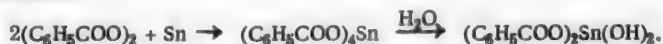
In the present work we have investigated the reaction of perbenzoic acid with stannous dichloride, antimony trichloride, and with metallic tin, and also the reaction of acetyl peroxide with antimony. It has previously been indicated that perbenzoic acid reacts with stannous dichloride but the reaction products were not isolated [4].

We investigated the reaction of stannous dichloride with peroxide dissolved in benzene, dichloroethane and acetic anhydride. Perbenzoic acid quantitatively reacted with stannous dichloride without evolution of CO_2 at ordinary temperatures according to the equation



By carrying out the reaction in benzene solution during heating, the perbenzoic acid reacted with stannous dichloride also, while only insignificant CO_2 evolution was observed at the same time. It is of interest to note that during the reaction of perbenzoic acid with metallic tin or with stannous dichloride in benzene during heating, the peroxide does not react at all with benzene. As preliminary experiments showed, antimony trichloride in benzene solution reacts analogously; the addition of the benzoate radicals to Sb^{III} proceeds with conversion into Sb^{V} . At the same time, the reaction of perbenzoic acid with benzene is suppressed.

Perbenzoic acid reacted with metallic tin during the heating in benzene solution. The benzoate radicals added to tin with the formation of the benzoate of tetravalent tin. However, this compound was shown to be very sensitive to the action of moisture and as a result of the reaction only a substance very close in analysis to the product of its hydrolysis could be isolated:



By heating perbenzoic acid with tin without solvent, the formation of tin benzoate also proceeds, but the greater portion of the peroxide is decomposed into diphenyl and CO_2 .

Acetyl peroxide readily reacts with metallic antimony during heating in benzene solution. The very readily hydrolyzed antimony acetate was isolated.

EXPERIMENTAL

Thermal Reaction of Perbenzoic Acid with Stannous Dichloride in Benzene

18.9 g (0.1 mole) of stannous chloride, 24.2 g (0.1 mole) of perbenzoic acid and 200 ml of benzene were simultaneously placed in a three necked flask with a stirrer. The reaction mass was heated to the boiling point of benzene while being stirred for 20 hours. Even a half-hour after the beginning of the experiment, the solution noticeably darkened. 0.09 g of CO_2 (2% of the theoretical) was evolved in the course of the experiment.

Upon completion of the reaction tests for peroxide and Sn^{II} gave negative results. After distilling off the benzene, a dark brown precipitate (43 g) remained; by saponification with hot benzene, 18.6 g of pure stannic dichlorodibenzoate was obtained or 43.1% of the theoretical. The solvent which was distilled off contained stannic chloride, the quantity of which was determined as AgCl . 1.1967 g of AgCl was obtained, which corresponded to 0.54 g of SnCl_4 .

Stannic dichlorodibenzoate dissolved on heating in chloroform, dichloroethane, and acetone, was poorly soluble in alcohol and benzene, and entirely insoluble in water. The substance did not melt at 330°. Benzoic acid was isolated by the action of hydrochloric acid. A small quantity of precipitate was heated in a test tube with concentrated hydrochloric acid until it dissolved. Benzoic acid with a m.p. of 119° was evolved. A mixed sample with pure benzoic acid had a m.p. of 120°. A precipitate of stannic sulfide settled out from the filtrate during the passage of hydrogen sulfide through it. The substance formed sodium benzoate as a result of the action of sodium hydroxide on it. Benzoic acid was also obtained by the action of steam on the stannic dichlorodibenzoate.

Found %: Cl 15.80; $C_{14}H_{10}O_4SnCl_2$. Calculated %: Cl 16.44. Found %: C 35.20, 34.65; H 2.73, 2.50; Sn 25.58, 26.40. $C_{14}H_{10}O_4SnCl_2$. Calculated %: C 38.91; H 2.31; Sn 27.49.

Reaction of Perbenzoic Acid with Stannous Chloride in Benzene Without Heating

6.3 g (0.033 mole) of anhydrous stannous chloride, 8.0 g (0.033 mole) of recrystallized perbenzoic acid and 50 ml of benzene were placed in a flask with a ground stopper. The mixture was shaken on a machine. Even a half hour after beginning the shaking the solution blackened. After shaking for 12 hours, all the peroxide had reacted. The benzene was distilled off from the reaction mixture. Tetravalent tin was determined in it. 0.6241 g of AgCl which corresponded to 0.28 g of $SnCl_4$ was obtained. The residue after distilling off the benzene weighed 14.0 g from which 4.82 g of pure $(C_6H_5COO)_2SnCl_2$ or 33.7% of the theoretical was isolated by washing off with hot benzene.

Reaction of Perbenzoic Acid With Stannous Chloride in Dichloroethane and in Acetic Anhydride Without Heating

The reaction was carried out in dichloroethane and also in acetic anhydride under the same conditions. 3.16 g (0.013 mole) of recrystallized perbenzoic acid, 2.46 g (0.013 mole) of stannous chloride and 50 ml of solvent were taken. The contents of the flask were shaken for 2 hours on a machine and then after distilling off the solvent 5.1 and 4.7 g of raw product respectively, was isolated. 1.69 g pure $(C_6H_5COO)_2SnCl_2$ was isolated from the 5.1 g of crude product. The solvent distilled off (dichloroethane and acetic anhydride) did not contain $SnCl_4$.

Thermal Reaction of Perbenzoic Acid With Antimony Trichloride in Benzene

By heating equimolecular quantities of antimony trichloride and perbenzoic acid in benzene the antimony was entirely converted from Sb^{III} into SbV . Noticeable quantities of CO_2 were not detected. During the treatment of the product obtained with hydrochloric acid the theoretical quantity of benzoic acid was evolved.

Thermal Reaction of Perbenzoic Acid With Metallic Tin in Benzene

250 ml of benzene and 10 g of powdered metallic tin were placed in a three-necked flask supplied with a mechanical stirrer with a mercury seal. The benzene was brought to boiling and during continuous stirring in the flask over a period of 4 hours, 20 g of perbenzoic acid (activity 93%) was introduced in small portions. The heating and stirring were continued for 13 more hours after this. Even a half hour after the beginning of the addition of the peroxide, darkening of the liquid was observed, which then became dark brown. Upon completion of the reaction a test for peroxide gave a negative result. Only traces of CO_2 were evolved during the reaction. The reaction mass consisted of a grey residue that was insoluble in benzene. The benzene layer was poured off from the residue, filtered and redistilled on a water bath. Alkali was added to the residue and steam passed through it. Upon completion of the steam distillation, the alkaline solution was filtered off, condensed to small volume after which it was acidified with hydrochloric acid. 1 g of benzoic acid with a m.p. of 121° (from water) was isolated. A mixed sample with pure benzoic acid gave a m.p. 121°. After the benzene had been separated from the water, it was subjected to redistillation, which demonstrated the absence of any other products in it. The grey precipitate obtained as a result of the reaction was filtered off and washed with benzene. It was shown to be poorly soluble in alcohol, acetone, ethylcellulose, ethyl ether, carbon tetrachloride, benzene, etc.. No appreciable changes were observed as a result of the action of caustic alkali or hydrochloric acid. The substance was shown to be rather soluble in dichloroethane and, therefore, it was subjected to extraction with this solvent in a Soxhlet apparatus. 14.3 g of a white crystalline substance was thus obtained which in analysis and properties fitted the formula $(C_6H_5COO)_2Sn(OH)_2$.

Found %: C 44.90, 45.08; H 2.90, 3.32; Sn 29.10, 29.80. $C_{14}H_{12}O_6Sn$. Calculated %: C 42.56; H 3.04; Sn 30.07.

This substance did not melt at temperatures up to 330°, however even at much lower temperatures cleavage of benzoic acid occurred, after which an infusible amorphous precipitate remained. The evolution of benzoic acid was observed as a result of the action of steam on this substance. Thus, 121 g of benzoic acid or 82.3% calculating on the basis of $(C_6H_5COO)_2Sn(OH)_2$ was obtained from a sample of 2.36 g. An analogous result was obtained by

preliminary alkalization of the sample. Benzoic acid was cleaved off by heating the precipitate with concentrated hydrochloric acid to 130-140° in a sealed tube.

Reaction of Perbenzoic Acid With Metallic Tin Without Heating

5 g of tin, 5 g of perbenzoic acid and 40 ml of benzene were shaken on a machine for 150 hours. The reactants were isolated unchanged.

Thermal Reaction of Perbenzoic Acid With Metallic Tin Without Solvent

0.1 g of perbenzoic acid with excess metallic tin was heated on a sand bath. The decomposition of the peroxide proceeded with detonation and evolution of CO₂. Crystals of diphenyl with a m.p. of 64-65° separated on the walls of the test tube on cooling. This substance was fused with pure diphenyl at 65°. The solid reaction products were extracted with dichloroethane. On evaporating off the dichloroethane a substance remained which was insoluble in the majority of organic solvents and was analogous to the substance from the experiment which was carried out in benzene solution with heating.

Thermal Reaction of Acetyl Peroxide With Metallic Antimony in Benzene*

10 g of metallic antimony and 8.7 g of acetyl peroxide in 100 ml of benzene were placed in a three-necked flask supplied with a mechanical stirrer with a mercury seal. The reaction mass was heated and stirred for 8 hours. 0.08 g of CO₂ was evolved in the course of the reaction. A test for the presence of peroxide gave a negative result. Colorless crystals separated on cooling the reaction mass, which were separated from the unreacted antimony (4.8 g). The crystals, which consisted of antimony triacetate, were transferred to a vacuum desiccator and dried. SbV ions were not found. This substance very rapidly underwent hydrolysis in air. The hydrolysis products consisted of antimony trioxide and acetic acid. The same sort of decomposition occurred during the action of aqueous alcohol. The antimony triacetate from the vacuum desiccator was treated with ethyl alcohol and back titrated with 0.1 N NaOH. 7.2 g of acetic acid was contained in it which was equivalent to 12.1 g of antimony triacetate. Thus, according to the triacetate formed, 4.9 g of antimony entered into the reaction. The quantity of antimony which reacted as found by the difference in the charge and in the residue was 5.1 g.

SUMMARY

1. Perbenzoic acid yields (C₆H₅COO)₂SnCl₂ with stannous chloride in benzene, dichloroethane and acetic anhydride solution. SbCl₃ reacts analogously.
2. Perbenzoic acid in benzene solution reacts with metallic tin during heating without CO₂ evolution, and with the formation of stannic tetrabenzoate. Its hydrolysis product (C₆H₅COO)₂Sn(OH)₂ was isolated.
3. Antimony triacetate was formed by heating antimony with a benzene solution of acetyl peroxide.

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Gorki State University

* E. A. Sheer completed the reaction of peroxide with Sb and SbCl₃.

** See Consultants Bureau Translation, page 613.

REACTION OF METHYL- α -NAPHTHYLMERCURY AND METHYLPHENYLMERCURY WITH ORGANIC ACIDS*

A. A. Bolshakova

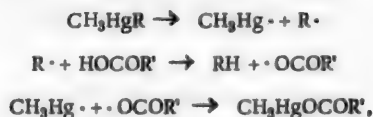
Cahours [1] and Otto [2] studied for the first time the reaction of alkyl and aryl compounds of mercury with acetic acid, and showed that the corresponding acetates and hydrocarbons were thereby formed. Melnikov and Rokitskaya [3] investigated the reaction of compounds of the R_2Hg type with mercury salts of dibasic and tribasic acids. Koton [4, 5] studied in great detail the reaction of diphenylmercury and di- α -naphthylmercury with monobasic organic acids, and gave as the general reaction equation



They further investigated [6] the reaction of dimethyl mercury with organic acids, and showed that, during heating for 3 hours at 130°, derivatives of the acids containing the $CH_3Hg\cdot$ radical were formed, and methane was evolved. Chernov [7, 8] studied the reaction of organic acids with di-o- and di-p-tolylmercury. He succeeded in all cases in observing the formation of derivatives of the $RHgOCOR'$ type where $RHg\cdot$ is the o- or p-tolylmercury radical, and the evolution of toluene.

It was of interest to study the reaction with organic acids of asymmetric organomercury compounds in the example of methyl- α -naphthylmercury and methylphenylmercury and to establish which of the radicals which enter into the composition of these compounds is the most reactive.

A crystalline substance with a definite melting point is formed during the reactions of methyl- α -naphthylmercury and methylphenylmercury with organic acids. The reaction proceeds during heating to 75° for 6 hours. On the basis of the experimental data, the mechanism of the reaction can be represented by the following scheme



where R' is the α -naphthyl or phenyl radical, while RH is, respectively, naphthalene or benzene. According to the analytical results, the derivatives obtained for dibasic acids contained two $CH_3Hg\cdot$ radicals and substituted hydrogens on both carboxyl groups. The experimental data permit one to conclude that the less reactive methyl radical remains bound to a mercury atom, and in such a form is transferred into the composition of the acid derivative. The more reactive α -naphthyl and phenyl radicals are torn off from the mercury and form naphthalene or benzene with a hydrogen atom. Consequently, the behavior of the methyl, α -naphthyl and phenyl radicals during the reactions of their asymmetric organomercury compounds is in complete agreement with the position of each of them in the Nesmeyanov-Kharasch series. It should also be noted that asymmetric compounds studied by us react with organic acids at a greater rate (even at 75°) than symmetric mercury compounds with which the reaction proceeds at 100 and 130°.

EXPERIMENTAL

I. Synthesis of Methyl- α -naphthylmercury and Methylphenylmercury

Methyl- α -naphthylmercury was synthesized by the method of Freidlina, Nesmeyanov and Kocheshkov [9]: it consisted of fine, colorless crystals with a m.p. of 82° (according to Nesmeyanov 84°).

0.0492 g sub.: 2.86 ml 0.1 N NH_4CNS . Found %: Hg 58.13. $C_{11}H_{10}Hg$. Calculated %: Hg 58.55.

Methylphenylmercury was prepared by the action of C_6H_5MgBr on CH_3HgI [10]. Methylphenylmercury is a heavy, transparent liquid. In view of the thermal instability of methylphenylmercury, its identification was carried out by treatment with an alcoholic solution of hydrogen chloride. Methylmercury chloride with a m.p. of 170-171° (according to the literature data 171°) was thereby quantitatively formed. A mixed sample with the known substance had a m.p. of 170°.

*Abstract from the candidate's dissertation of A. A. Bolshakova.

All the experiments involving the study of the reaction of mercury compounds with organic acids were carried out in sealed glass ampoules during heating to 75° for 6 hours.

II. Reaction of Methyl- α -naphthylmercury with Organic Acids

1. Stearic acid. 0.15 g stearic acid and 0.2 g of methyl- α -naphthylmercury were taken. With benzene 0.06 g of a white substance with a m.p. of 80-81° was isolated.

0.0510 g sub.: 2.03 ml 0.1 N NH_4CNS . Found %: Hg 39.80. $\text{C}_{17}\text{H}_{35}\text{COOHgCH}_3$. Calculated %: Hg 40.23.

2. Adipic acid. The mixture was heated for 3 hours at 100°. 0.1 g of adipic acid was taken for 0.2 g of methyl- α -naphthylmercury. With hot water 0.06 g of a white crystalline substance with a m.p. of 171-173° was isolated.

0.0500 g sub.: 3.48 ml 0.1 N NH_4CNS . Found %: Hg 69.60. $(\text{CH}_2)_4(\text{COOHgCH}_3)_2$. Calculated %: Hg 69.73.

3. Salicylic acid. 0.1 g of salicylic acid was taken for 0.2 g of methyl- α -naphthylmercury. With hot aqueous alcohol 0.05 g of a white crystalline substance with a m.p. of 112-114° was obtained.

0.0350 g sub.: 1.98 ml 0.1 N NH_4CNS . Found %: Hg 56.57. $\text{C}_6\text{H}_4(\text{OH})\text{COOHgCH}_3$. Calculated %: Hg 56.89.

4. Phthalic acid. 0.1 g of phthalic acid and 1 drop of water were taken for 0.2 g of methyl- α -naphthylmercury. With hot alcohol 0.07 g of a crystalline substance with a m.p. of 223-224°, with decomposition, was isolated.

0.0512 g sub.: 3.45 ml 0.1 N NH_4CNS . Found %: Hg 67.18. $\text{C}_6\text{H}_4(\text{COOHgCH}_3)_2$. Calculated %: Hg 67.44.

Naphthalene was detected in all the experiments, and its presence demonstrated in the usual way.

III. Reaction of Methylphenylmercury with Organic Acids

1. Butyric acid. 0.5 ml of butyric acid was taken for 0.15 g methylphenylmercury. The reaction mass was a liquid. On adding water white flaky crystals separated from the reaction mass on standing. After recrystallization from alcohol 0.04 g of white flaky crystals with a m.p. of 44-45° was obtained.

0.0330 g sub.: 1.98 ml 0.1 N NH_4CNS . Found %: Hg 66.00. $\text{CH}_3(\text{CH}_2)_2\text{COOHgCH}_3$. Calculated %: Hg 66.29.

2. α -Hydroxybutyric acid. 0.5 ml of α -hydroxybutyric acid was taken for 0.15 g of methylphenylmercury. 0.09 g of a white crystalline substance with a m.p. of 96-97° was isolated with water from the reaction mass during prolonged standing.

0.0500 g sub.: 3.14 ml 0.1 N NH_4CNS . Found %: Hg 62.80. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOHgCH}_3$. Calculated %: Hg 62.96.

3. Nonylic acid. 0.5 ml of nonylic acid was taken for 0.15 g of methylphenylmercury. 0.1 g of yellowish crystals with a m.p. of 45-46° was isolated from the reaction mixture.

0.0500 g sub.: 2.49 ml 0.1 N NH_4CNS . Found %: Hg 49.80. $\text{CH}_3(\text{CH}_2)_7\text{COOHgCH}_3$. Calculated %: Hg 50.58.

4. Palmitic acid. 0.15 g of palmitic acid was taken for 0.15 g of methylphenylmercury. 0.11 g of a white substance with a m.p. of 72-73° was isolated with hot alcohol.

0.0500 g sub.: 2.11 ml 0.1 N NH_4CNS . Found %: Hg 42.20. $\text{C}_{15}\text{H}_{31}\text{COOHgCH}_3$. Calculated %: Hg 42.62.

5. Stearic acid. 0.15 g of stearic acid was taken for 0.15 g of methylphenylmercury. 0.1 g of a white substance with a m.p. of 80-81° was isolated with hot alcohol.

0.0500 g sub.: 2.00 ml 0.1 N NH_4CNS . Found %: Hg 40.00. $\text{C}_{17}\text{H}_{35}\text{COOHgCH}_3$. Calculated %: Hg 40.23.

6. Adipic acid. 0.2 g of adipic acid was taken for 0.2 g of methylphenylmercury. 0.1 g of a white crystalline substance with a m.p. of 171-173° was isolated with hot water.

0.0500 g sub.: 3.47 ml 0.1 N NH_4CNS . Found %: Hg 69.40. $(\text{CH}_2)_4(\text{COOHgCH}_3)_2$. Calculated %: Hg 69.74.

7. Citric acid. 0.15 g of citric acid was taken for 0.15 g of methylphenylmercury. Heating was continued for 1 hour at 100°. 0.09 g of a white crystalline substance which decomposed at 139° was isolated with alcohol.

0.0520 g sub.: 3.33 ml 0.1 N NH_4CNS . Found %: Hg 64.04. $\text{C}(\text{OH})(\text{COOH})(\text{CH}_2\text{COOHgCH}_3)_2$. Calculated %: Hg 64.58.

8. Benzoic acid. 0.1 g of benzoic acid was taken for 0.15 g of methylphenylmercury. 0.09 g of a white crystalline substance with a m.p. of 105-106° was isolated with ether.

0.0500 g sub.: 2.97 ml 0.1 N NH_4CNS . Found %: Hg 59.40. $\text{C}_6\text{H}_5\text{COOHgCH}_3$. Calculated %: Hg 59.59.

9. Salicylic acid. 0.15 g of salicylic acid was taken for 0.2 g of methylphenylmercury. 0.11 g of white crystals with a m.p. of 112-114° was isolated.

0.0500 g sub.: 2.82 ml 0.1 N NH_4CNS . Found %: Hg 56.40. $\text{C}_6\text{H}_4(\text{OH})\text{COOHgCH}_3$. Calculated %: Hg 56.89.

10. Phthalic acid. 0.1 g of phthalic acid was taken for 0.15 g of methylphenylmercury. 0.19 g of a white crystalline substance which melted at 223-224°, with decomposition, was isolated with hot alcohol.

0.0600 g sub.: 4.03 ml 0.1 N NH_4CNS . Found %: Hg 67.17. $\text{C}_6\text{H}_4(\text{COOHgCH}_3)_2$. Calculated %: Hg 67.44.

The reaction products of methylphenylmercury with stearic, adipic, salicylic and phthalic acids were the same as those obtained during the reaction of methyl- α -naphthylmercury with the acids named.

I convey my heartfelt gratitude to M. M. Koton for submitting the theme for the dissertation and for guidance during the completion of the work.

SUMMARY

1. Methyl- α -naphthylmercury and methylphenylmercury form crystalline derivatives of the general formula CH_3HgOOCR during reaction with monovalent acids.

2. Methyl- α -naphthylmercury and methylphenylmercury form crystalline derivatives of the general formula $\text{CH}_3\text{HgOOCRCOOHgCH}_3$ with dibasic acids.

3. During the reaction of asymmetric compounds of mercury with organic acids, the more reactive radical (naphthyl, phenyl), is first split off to form a hydrocarbon (naphthalene, benzene) with the hydrogen of the acid and the free radicals which are formed then yield the corresponding acyl derivatives.

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* See Consultants Bureau Translation, page 1181.

** See Consultants Bureau Translation, page 345.

*** See Consultants Bureau Translation, page 113.



DESTRUCTIVE HYDROGENATION OF TETRAETHYLSILANE

M. G. Voronkov, B. N. Dolgov and G. B. Karpenko

It was shown a quarter of a century ago by one of the authors [1] that tetraethylsilane when heated to 350-360° under hydrogen pressure, cleaves off ethane and is converted into hexaethyldisilane



The formation of silane and, apparently, of higher ethylated silanes is observed along with this.

The hydrogenation of tetraethylsilane in the vapor phase at ordinary pressure was investigated in the present work. It was established in the course of this work that tetraethylsilane is not altered at temperatures up to 500° in an atmosphere of hydrogen in the absence of catalyst. At higher temperatures pyrolysis of the tetraethylsilane proceeds [2] with formation of elementary silicon and gaseous products, and the reaction chiefly proceeds according to the equation $\text{Si}(\text{C}_2\text{H}_5)_4 \rightarrow \text{Si} + 4\text{C}_2\text{H}_4 + 2\text{H}_2$. Ethylene pyrolysis products—methane and carbon—are formed simultaneously.

We found during the study of the reaction of tetraethylsilane with hydrogen over various catalysts that over active aluminum silicate catalyst at a temperature close to the initial pyrolysis temperature of tetraethylsilane (550°), its destructive hydrogenation into triethylsilane proceeds:



Along with the destructive hydrogenation of tetraethylsilane into triethylsilane, a more profound hydrogenolysis also proceeds with formation of elementary silicon, deposited on the catalyst, and ethane: $\text{Si}(\text{C}_2\text{H}_5)_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{C}_2\text{H}_6$.

This reaction becomes predominant when the temperature is increased above 600°. At the optimal temperature (550°) the destructive hydrogenation of tetraethylsilane over aluminum silicate catalyst leads to the formation of up to 55% of triethylsilane, calculating on the basis of the condensate obtained. The latter consists of a mixture of $\text{Si}(\text{C}_2\text{H}_5)_4$ and $\text{HSi}(\text{C}_2\text{H}_5)_3$. No other volatile reaction products which condensed at -80° were isolated during the hydrogenolysis of tetraethylsilane over aluminum silicate catalyst. Thus, neither hexaethyldisilane (the product of the hydrogenation of $\text{Si}(\text{C}_2\text{H}_5)_4$ under pressure, nor the ethylsilanes $(\text{C}_2\text{H}_5)_2\text{SiH}_2$ and $(\text{C}_2\text{H}_5)_3\text{SiH}_3$ were formed during the destructive hydrogenation of tetraethylsilane. Ethylene—the product of the pyrolysis of tetraethylsilane in the absence of catalyst—was also absent.

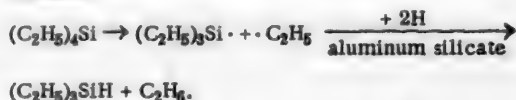
The dependence of the yield of triethylsilane on the temperature of the hydrogenation of tetraethylsilane over industrial and synthetic aluminum silicate catalyst is presented in Table 1. These data show that the optimal yield of triethylsilane for both catalysts occurs at 550°; the industrial sample of aluminum silicate catalyst appears to be more active.

TABLE 1
Yields of Triethylsilane During the Destructive Hydrogenation of Tetraethylsilane Over Aluminum Silicate Catalyst

Temp. (in °)	Yield of triethylsilane (in %), calculating on the basis of the initial $\text{Si}(\text{C}_2\text{H}_5)_4$ *	
	Industrial catalyst	Synthetic catalyst
350	0	0
400	6	0
450	11	0
500	25	6
530	—	25
550	54	32
580	—	28
600	14	15

* Average of analytical determinations by three methods.

The reaction mechanism of the destructive hydrogenation can be represented by the following scheme:



It follows from this scheme that the $(\text{C}_2\text{H}_5)_3\text{Si} \cdot$ and $\cdot\text{C}_2\text{H}_5$ radicals formed as a result of the pyrolysis are hydrogenated at the surface of the catalyst. In the absence of catalyst, these radicals are decomposed into silicon, ethylene and hydrogen [2], while under hydrogen pressure, they are converted into hexaethyldisilane and ethane. At a high tetraethylsilane hydrogenolysis temperature

the triethylsilyl radical is decomposed:



The ethyl radicals thereby formed are hydrogenated on the catalyst to ethane while the silicon is not changed (as is well known, silicon hardly reacts with hydrogen [3]; silane is completely decomposed into its elements at a temperature above 380° [4]).

EXPERIMENTAL

Tetraethylsilane was obtained in a yield of 83% by the reaction of $\text{C}_2\text{H}_5\text{MgCl}$ with silicon chloride and was carefully purified by Eger's method [5]. After redistillation in a column over sodium it had the following constants: b.p. 152° (760 mm); d_4^{20} 0.7657; n_D^{20} 1.4268.

Triethylsilane was obtained in a yield of 75% by the reaction of $\text{C}_2\text{H}_5\text{MgCl}$ with trichlorosilane [6]. After treatment with sodium in the cold, it was distilled in a column. Its constants were: b.p. 108.0° (756 mm); d_4^{20} 0.7311; n_D^{20} 1.4121.

Catalyst. Industrial aluminum silicate catalyst was used as well as catalyst prepared by the method described in the literature. The latter catalyst turned out to be less effective. The application of nickel, iron and copper to the aluminum silicate catalyst led to lowering the yields of triethylsilane during the destructive hydrogenation of tetraethylsilane.

Experimental methods. The destructive hydrogenation of tetraethylsilane was carried out by a circulating method in the usual catalytic apparatus. Granulated catalyst (volume 75 ml) was placed in a pyrex tube with an internal diameter of 20 mm. The length of the catalyst layer was 28 cm. The catalyst was preliminarily heated in a rapid stream of hydrogen at 450° until the evolution of water had entirely ceased. The tetraethylsilane was passed over the catalyst at a rate of 10 ml/hour, (volumetric rate 16) in a stream of pure dry hydrogen (6 liters/hour). The liquid reaction products were collected in a receiving flask cooled to 0° and supplied with a reflux condenser. The gases formed during the reaction did not contain components which condensed into two successively placed traps which were cooled to -80°. They also did not contain unsaturated compounds or silane (the absence of a reaction with bromine solution and KMnO_4) and consisted of ethane and hydrogen. Regeneration of the catalyst was carried out after every 6-8 experiments by passing a stream of dry air through the catalyst, which was heated to 450° until it became white. The activity of the catalyst nevertheless, was somewhat lowered (apparently due to shielding of the active centers with silicon dioxide which was formed by the oxidation of the silicon which was deposited on the catalyst). The experimental data are set forth in Table 1.

Method of analysis. In preliminary experiments the catalyzate was distilled in an analytical column. In all cases it consisted of a two component mixture of triethylsilane and unchanged tetraethylsilane. The triethylsilane isolated during the fractional distillation of the catalyzate had a b.p. of 107.3-108.3°; d_4^{20} 0.7299; n_D^{20} 1.4119.

Found M: 116.4, 117.5. $\text{C}_6\text{H}_{16}\text{Si}$. Calculated M: 116.28. Found %: H (Si) 0.85, 0.86. $(\text{C}_2\text{H}_5)_3\text{SiH}$. Calculated %: H (Si) 0.87.

The absence in the catalyzate of any other compounds besides $\text{Si}(\text{C}_2\text{H}_5)_4$ and $\text{HSi}(\text{C}_2\text{H}_5)_3$ (including resinification products) made it possible to analyze the catalyzate more fully for triethylsilane content. Three methods were used for this.

1) **Content in the catalyzate of hydrogen bound to silicon.** The determination of the hydrogen bound to silicon in the triethylsilane was carried out by splitting the Si-H bond with alcoholic alkali [7] or with sulfuric acid containing HgSO_4 . The hydrogen evolved by this treatment of a catalyzate sample was collected and measured in a gas burette over mercury.

2) **Elimination of triethylsilane from the catalyzate by sulfuric acid.** We found that triethylsilane is readily and completely dissolved in concentrated sulfuric acid with the evolution of hydrogen, and is thereby converted into the H_2SO_4 soluble bis-(triethylsilane)-sulfate and hexaethyldisiloxane. This reaction is catalyzed by mercury salts. In contrast to this, tetraethylsilane is practically insoluble in concentrated H_2SO_4 (0.8 + 0.2 ml of $(\text{C}_2\text{H}_5)_4\text{Si}$ dissolve in 100 ml of sulfuric acid at 20°). The determination of the content of triethylsilane in the catalyzate treated with sulfuric acid was carried out in a sulfato-burette by the method customarily used in hydrocarbon analysis. The method was verified by artificial mixtures of tetraethylsilane and triethylsilane. In each determination, 5 ml of concentrated H_2SO_4 containing 0.5% HgSO_4 was taken and an experimentally found correction factor was introduced for the solubility of tetraethylsilane.

3) **Refractive index of the catalyzate.** We determined the refractive indices (n_D^{20}) of binary mixtures of triethylsilane and tetraethylsilane. These data, presented in Table 2, show that within the limits of the error of measurement, the dependence between triethylsilane content in the mixture (in percentages by weight) and its

TABLE 2

Refractive Indices of Binary Mixtures of Tetraethylsilane-Triethylsilane

Content of (C ₂ H ₅) ₄ SiH (in % by weight)	n_D^{20} + 0.0002
0.0	1.4268
25.7	1.4229
28.4	1.4227
34.0	1.4216
43.0	1.4206
49.9	1.4195
56.4	1.4186
67.5	1.4170
71.1	1.4162
80.2	1.4151
91.9	1.4132
100.0	1.4121

refractive index is determined by the linear equation: $\% (C_2H_5)_3SiH = 6803 (n_D^{20} - 1.4268)$. This equation was employed to determine the triethylsilane content in the catalyzate by its refractive index.

A number of experiments which we carried out under various conditions using various solvents for the volumetric determination of triethylsilane iodometrically, mercurimetrically and argentometrically, did not lead to satisfactory enough results.

SUMMARY

It was shown that at a temperature close to 550°, tetraethylsilane is cleaved by hydrogen over aluminum silicate catalyst with formation of triethylsilane and ethane.

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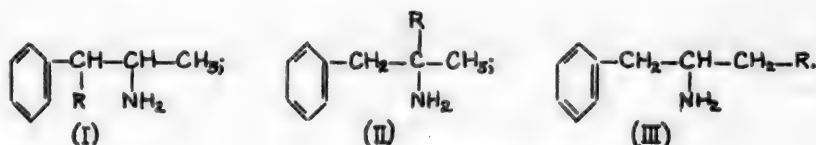
USE THIS SIDE

SYNTHESIS OF CERTAIN PHENAMINE DERIVATIVES

F. Yu. Rachinsky and N. M. Vinokurova

Phenamine derivatives as nervous system stimulants have up to now attracted the attention of pharmacologists, who have tried to establish a relation between the structure and the physiological activity of the given series of compounds.

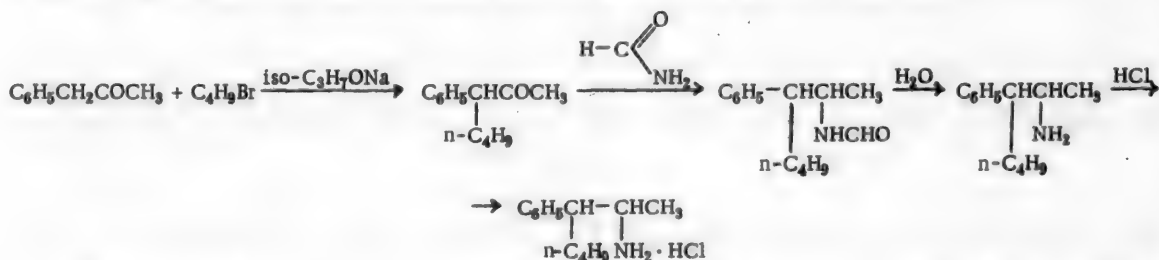
To resolve this problem, the synthesis of phenamine derivatives with an elongated side carbon chain was accomplished



The first member of each series was distinguished from the next following member only by the homologous difference which permitted the influence of separate functional groups of the substance on its physiological activity to be established.

In Table 1 are set forth data on the phenamine derivatives synthesized by us, including two compounds obtained for the first time and characterized by us — a compound with the butyl radical on the first carbon atom of the side chain and one with an isobutyl radical on the second carbon atom (Table 1, Nos. 4 and 10).

The phenamine derivative with the butyl radical on the first carbon atom was prepared from methylbenzyl ketone by the Leuckart reaction extended by Suter and Weston [1] to alkylphenylacetones.



The hydrochloride of 2-amino-3-phenylheptane was isolated in two diastereoisomeric forms with m.p. of 148-149 and of 228°; the possibility of the formation of which was due to the presence of two asymmetric carbon atoms.

Along with the low melting form of the hydrochloride (obtained in experiment No. 1) (m.p. 136-139°) described in the literature, a high melting form of the hydrochloride (m.p. 212-212.5°) was isolated. The methyl derivative of the given series — 2-amino-3-phenylbutane was also obtained in two diastereoisomeric forms. With the exception of the phenyl derivative, all the phenamine derivatives with elongated side chains at the first carbon atom were synthesized from the corresponding ketones by the scheme set forth above.

The phenyl derivative was prepared from methylbenzyl ketone by reduction of the ketoxime with metallic sodium in absolute ethyl alcohol

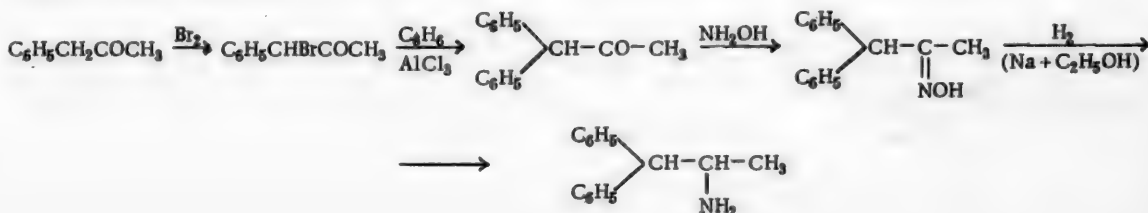


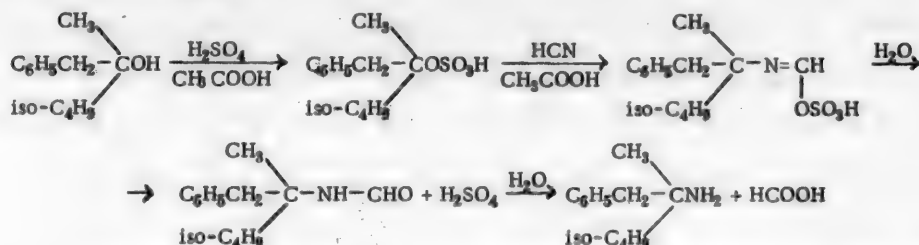
TABLE 1

Expt. No.	Formula of the amine	Boiling point (in °) at pressure (in mm)	Melting point of the hydrochloride (in °)	Literature data	
				Boiling point (in °) at pressure (in mm)	Melting point of the hydrochloride (in °)
1	$\text{C}_6\text{H}_5-\text{CH}-\text{CH}-\text{CH}_3$ [1] $\text{CH}_3 \quad \text{NH}_2$	100-105 (13)	1) 212-212.5 2) 137-138**	118-119 (19)	136-139
2	$\text{C}_6\text{H}_5-\text{CH}-\text{CH}-\text{CH}_3$ [1] $\text{C}_2\text{H}_5 \quad \text{NH}_2$	107-110 (18)	172-173	118 (19)	1) 171-172 2) 258-261**
3	$\text{C}_6\text{H}_5-\text{CH}-\text{CH}-\text{CH}_3$ [1] $n\text{-C}_3\text{H}_7 \quad \text{NH}_2$	102-103 (7)	249-250	116 (15)	1) 250-253 2) 120-123**
4	$\text{C}_6\text{H}_5-\text{CH}-\text{CH}-\text{CH}_3$ • $n\text{-C}_4\text{H}_9 \quad \text{NH}_2$	120 (8)	1) 228 2) 148-149**	—	—
5	$\text{C}_6\text{H}_5-\text{CH}-\text{CH}-\text{CH}_3$ [2] $\text{C}_6\text{H}_5 \quad \text{NH}_2$	174-180 (20)	278	176-179 (21-23)	280-282
6	$\text{C}_6\text{H}_5-\text{CH}_2-\text{C}-\text{CH}_3$ [3] CH_3 NH_2	65 (3)	198	85-90 (10)	198-198.5
7	$\text{C}_6\text{H}_5-\text{CH}_2-\text{C}-\text{CH}_3$ [4] C_2H_5 NH_2 $n\text{-C}_3\text{H}_7$	114 (19)	200		200-201
8	$\text{C}_6\text{H}_5-\text{CH}_2-\text{C}-\text{CH}_3$ [5] NH_2 $n\text{-C}_4\text{H}_9$	118 (10)	161	118 (10)	161
9	$\text{C}_6\text{H}_5-\text{CH}_2-\text{C}-\text{CH}_3$ NH_2 $\text{iso-C}_4\text{H}_9$	115 (6)	Not obtained in the crystalline form	115 (6)	Not obtained in the crystalline form
10	$\text{C}_6\text{H}_5-\text{CH}_2-\text{C}-\text{CH}_3$ • NH_2	113-114 (14)		—	—
11	$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3$ [5] NH_2	104-113 (6)	141		146
12	$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}_2\text{H}_5$ [5] NH_2	102-104 (9)	125-126		131
13	$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}_6\text{H}_5$ [6] NH_2	189-193 (13) m.p. 48-49	200	117 (12), m.p. 50	200-202

• Prepared for the first time.

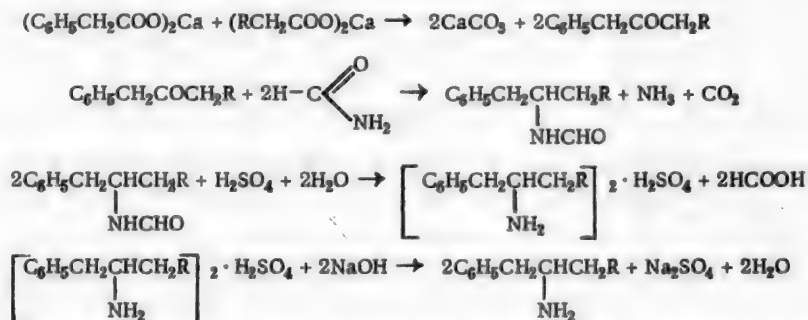
** Diastereoisomeric forms.

The phenamine derivative with the isobutyl radical at the second carbon atom was prepared by Ritter and Kalisch's reaction [3]:



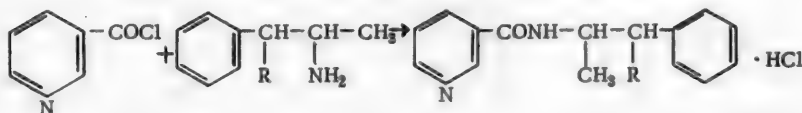
Other phenamine derivatives with substituents at the second carbon atom were also synthesized by this reaction.

The synthesis of phenamine derivatives with an elongated side chain at the third carbon atom was accomplished by us by Leuckart's reaction under the conditions described by Magidson and Garkusha [7]. The entire synthetic process can be depicted by the following scheme



The pharmacological investigation of the phenamine derivatives showed that the position of the radical on any particular carbon atom of the side chain did not exert significant influence on the change of the properties of the preparation.

The weight of the radical and the substitution of a phenyl radical for an alkyl radical substantially affected the pharmacological activity of the preparation. The phenyl derivative had a more pronounced stimulative action in comparison with phenamine and its alkyl derivatives. With increasing weight of the radical (by substitution in positions 1, 2, and 3) the stimulant action on the sympathetic nervous system disappears. Several of the derivatives synthesized by the condensation of nicotinic acid chloride with phenamine were converted into the corresponding amides [8]



In Table 2, the nicotinic acid amides obtained by us are set forth.

The amides consisted of solid, colorless crystalline substances or thick, yellowish oils which solidified in the cold into a vitreous mass and crystallized on prolonged standing. The amides were insoluble in water and readily soluble in benzene, dioxane, chloroform, ether, alcohol, and peach oil. The solubility of the phenyl derivative was less.

The amides were converted into the salts of hydrochloric and phosphoric acids for pharmacological investigation. Only the hydrochloride and phosphate of the methyl derivative (second carbon atom) were isolated in the crystalline state; they were readily soluble in water. The salts of the phenyl derivative did not dissolve in water and the salts of the other amides were not obtained in the crystalline form.

TABLE 2

Expt. No.	Formula of the amides	Temperature		Molecular weight of the amide		Nitrogen content (in %)		Notes
		Boiling point of the amide (in °) at pressure (in mm)	Melting point of the amide (in °)	Found	Calculated	Found	Calculated	
1		238 (15)	Does not crystallize	251.3	254	11.12	11.02	Salts not obtained in the crystalline form
2		235-237 (15)	78-80	292.5	296	9.74	9.46	
3		—	94	258.8	254	11.40	11.02	Salts (hydrochloride and phosphate) obtained in the crystalline state
4		—	100-101	270.2	268	10.21	10.44	
5		232-234 (13)	Does not crystallize	293	296	9.62	9.46	Salts not obtained in the crystalline form
6		239 (16)		293	296	9.52	9.46	
7		—	176	—	—	9.22	8.86	Salts did not dissolve in water

EXPERIMENTAL

I. Synthesis of Phenamine Derivatives

1. Synthesis of 2-amino-3-phenylheptane (Table 1, No. 4)

α -Butyl- α -phenylacetone was prepared by the alkylation of phenylacetone in the presence of sodium isopropylate. 9.2 g (0.4 mole) of metallic sodium was introduced in small fragments into a solution of 53.6 g (0.4 mole) of phenylacetone and 300 ml of dry isopropyl alcohol. After the formation of the sodium isopropylate, 73.6 g (0.4 mole) of butyl iodide was added in drops. The contents of the flask were heated for 2 hours, the alcohol was distilled off, the residue diluted with water, and the ketone which was evolved was extracted with ether. After distilling off the ether, the ketone was vacuum distilled (15 mm). 25 g of α -butyl- α -phenylacetone was isolated by repeated fractional distillation:

b.p. 116° (15 mm); n_D^{20} 1.50342; d_4^{20} 0.9597; MR_D 58.56. $C_{13}H_{18}O$; calculated 58.64.

The formyl derivative was prepared by heating 42 g of α -butyl- α -phenylacetone and 50 g of formamide for 16 hours at a temperature of 180-205°.

The following fractions were obtained by vacuum distilling the mixture (13 mm): 1st b.p. 96-114°, 31 g (a stratified liquid consisting of ketone and formamide); 2nd b.p. 114-200°, 5 g; 3rd b.p. 200-203°, 14 g.

The third fraction corresponded to the formyl derivative and was a viscous liquid which crystallized on standing:

b.p. 200-203° (13 mm); n_D^{20} 1.51326; d_4^{20} 0.9922; MR_D 66.39. $C_{14}H_{21}ON$; calculated 66.86.

0.2280 g sub.: 10.6 ml 0.1 N H_2SO_4 (Kjeldahl). Found % N 6.50. $C_{14}H_{21}ON$. Calculated %: N 6.39.

0.2246 g sub.: 16.76 g benzene: Δt 0.312°. Found: M 220.3. $C_{14}H_{21}ON$. Calculated: M 219.

2-Amino-3-phenylheptane was obtained by the hydrolysis of the formyl derivative (55 g) by energetic boiling with concentrated HCl (100 ml) for 24 hours; the mixture was diluted with water, the unreacted formyl derivative extracted with ether, the amine isolated with solid alkali and extracted with ether. After distilling off the ether, the amine was vacuum distilled. 35 g (73%) of the amine was obtained:

b.p. 114-115° (13 mm); n_D^{20} 1.50675; d_4^{20} 0.9166; MR_D 61.97. $C_{13}H_{21}N$; calculated 62.06.

0.4000 g sub.: 21.4 ml 0.1 N H_2SO_4 (Kjeldahl). 0.1812 g sub.: 15.11 g benzene: Δt 0.32°. Found %: N 7.49; M 192. $C_{13}H_{21}N$. Calculated %: N 7.32; M 191.

The hydrochloride of 2-amino-3-phenylheptane was prepared by saturating a solution of 35 g of the amine in dry ether with dry gaseous HCl. 40.2 g (96%) of the salt was obtained. A portion of the salt was subjected to fractional recrystallization from benzene. Well formed crystals were isolated - parallelepipeds with a m.p. of 148-149°.

0.1804 g sub.: 7.9 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 15.53. $C_{13}H_{22}NCl$. Calculated %: Cl 15.60.

Another portion of the salt was subjected to fractional crystallization from methyl alcohol with ether. A crystalline substance with a m.p. of 228° was isolated.

0.2018 g sub.: 8.8 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 15.46. $C_{13}H_{22}NCl$. Calculated %: Cl 15.60.

2. Synthesis of 2-amino-3-phenylbutane (Table 1, No. 1)

The synthesis was carried out analogously to that of 2-amino-3-phenylheptane. By fractional crystallization from methyl alcohol with ether, along with the low-melting form of the hydrochloride with a m.p. of 137-138°, a high-melting form was isolated with a m.p. of 212-212.5°.

0.1124 g sub.: 6.05 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 19.08. $C_{10}H_{16}NCl$. Calculated %: Cl 19.13.

3. Synthesis of 2-amino-2,4-dimethyl-1-phenylpentane (Table 1, No. 10)

Formyl derivative. 27.7 g of KCN and 48.6 ml of glacial acetic acid were stirred while being cooled in a three-necked flask supplied with a mechanical stirrer and a reflux condenser. 97.2 g of concentrated H_2SO_4 in 48.6 ml of glacial acetic acid was added in drops to the mixture. The temperature was kept below 20°. 77 g of methylisobutylbenzylcarbinol was added to the reaction mixture. The contents of the flask were heated for 30 minutes on a water bath at a temperature of 70° and left for a day, after which they were poured out into 500 ml of water and neutralized with soda. The oily layer which separated was extracted with ether and the ethereal solution dried with anhydrous Na_2SO_4 . After distilling off the ether and distilling the residue in a vacuum, 45 g of a substance in the form of a thick, yellowish oil, which crystallized on standing, was obtained:

m.p. 72-73°, b.p. 210° (15 mm).

0.3018 g sub.: 14.0 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.49. $\text{C}_{14}\text{H}_{21}\text{ON}$. Calculated %: N 6.39.

2-Amino-2,4-dimethyl-1-phenylpentane. 45 g of the formyl derivative was boiled energetically with concentrated HCl (80 ml) for 16 hours. After the usual processing 30 g of the amine was obtained:

b.p. 113-114° (14 mm); n_D^{20} 1.5084; d_4^{20} 0.9219; M_R 61.77. $\text{C}_{13}\text{H}_{21}\text{N}$; calculated 62.06.

0.3310 g sub.: 16.8 ml 0.1 N H_2SO_4 (Kjeldahl). 0.5400 g sub.: 14.40 g benzene: Δt 1.02°. Found %: N 7.10. M 188. $\text{C}_{13}\text{H}_{21}\text{N}$. Calculated %: N 7.32; M 191.

Hydrochloride of the amine. By passing dry gaseous HCl through the ethereal solution, an oil was formed (which did not crystallize).

II. Preparation of the Amides of Nicotinic Acid

A description of the standard method of preparing the amides is set forth below. The properties and analytical data of the amides are set forth in Table 2.

Condensation of 1-phenyl-2-methyl-2-aminopropane with nicotinic acid chloride

A solution of 14.2 g (0.1 mole) of nicotinic acid chloride in 30 ml of benzene was introduced dropwise into a solution of 14.9 g (0.1 mole) of the amine in 30 ml of dry benzene placed in a round bottomed flask supplied with a mechanical stirrer, a reflux condenser and a dropping funnel, after which the mixture was heated for 3 hours at a temperature of 80°. The solution turned brown and the condensation product precipitated in the form of a thick precipitate which was filtered off, washed with benzene, alcohol with ether, and dried. After recrystallization from alcohol, regularly formed, hexagonally shaped crystals with a m.p. of 180° were obtained. The weight was 16 g (55%).

0.1274 g sub.: 4.44 ml 0.1 N AgNO_3 (Volhard). Found %: Cl 12.35. $\text{C}_{16}\text{H}_{19}\text{ON}_2\text{Cl}$. Calculated %: Cl 12.22.

The hydrochloride dissolved in water, alcohol and chloroform in the cold. The solution of the hydrochloride in water was treated with sodium hydroxide to isolate the free amide; the crystalline substance which separated was filtered off, washed carefully with water and dried. After recrystallization from benzene, regularly formed prismatically shaped crystals were obtained with a m.p. of 94°.

0.0834 g sub.: 8.0 ml N_2 (16°, 766.8 mm). 0.1400 g sub.: 16.30 g benzene: Δt 0.170°. Found %: N 11.40; M 238.2. $\text{C}_{16}\text{H}_{19}\text{ON}_2$. Calculated %: N 11.02; M 254.

The amide did not dissolve in water. It dissolved in the cold in benzene, ether, acetone, alcohol, chloroform and other organic solvents.

The phosphate was obtained in crystalline form by stirring an alcoholic solution of phosphoric acid (2 moles) with an alcoholic solution of the amide (1 mole) (anhydrous ether was added to initiate the crystallization). After recrystallization from anhydrous ethyl alcohol, the m.p. was 145° and the substance readily dissolved in water.

0.0399 g sub.: 40.15 ml 0.1 N NaOH. Found %: H_3PO_4 . 42.90. $\text{C}_{16}\text{H}_{19}\text{ON}_2 \cdot 2\text{H}_3\text{PO}_4$. Calculated %: H_3PO_4 43.55.

SUMMARY

1. 13 phenamine derivatives with elongated carbon side chains were synthesized. The phenyl derivative appeared to be a more active nervous system stimulant than phenamine.
2. The synthesis and properties of two new phenamine derivatives were described: 2-amino-3-phenylheptane and 2-amino-2,4-dimethyl-1-phenylpentane.
3. The synthesis and properties of seven new amides of nicotinic acid which were of therapeutic significance were described.

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SEVERAL BENZOTHAZOLE DERIVATIVES

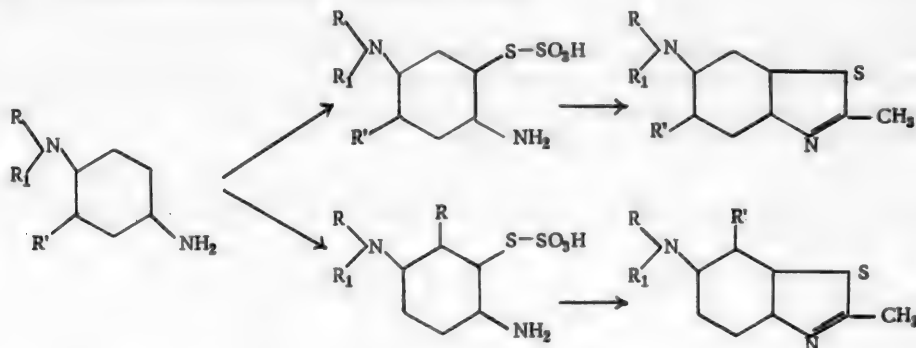
V. SYNTHESIS OF 5-SUBSTITUTED 6-DIMETHYLAMINO-2-METHYLBENZOTHAZOLES

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6-Dialkylamino-2-alkylbenzothiazoles were synthesized for the first time by the action of the acid chlorides or anhydrides of carboxylic acids on p-amino-m-mercaptodialkylanilines or their salts [1, 2]. Later Kiprianov and Sych showed [3] that 2-methyl-6-dialkylaminobenzothiazoles are readily formed by heating the accessible p-amino-dialkylaniline-m-thiosulfonic acids with acetic anhydride and acetic acid [4] (cf. also [10]).

It seemed expedient to use this method to obtain 2-methyl-6-mono- and dialkylaminobenzothiazoles, which contained various substituents in the hetero radical, via the conversion of substituted p-aminomono- and dialkylanilines into the corresponding thiosulfonic acids, with subsequent treatment of the latter or their reduction products with acetic anhydride.

In the case of o-substituted p-aminomono- or dialkylanilines it could be expected during their acidification in mixtures with thiosulfates that two isomeric thiosulfonic acids and their corresponding 5- and 7-substituted 2-methyl-6-mono- or dialkylaminobenzothiazoles would be formed



R - alkyl; R₁ - H or alkyl; R' - substituting group

In the present work we investigated the preparation of thiosulfonic acids from o-methoxy-, o-chloro- and o-dimethylamino-p-aminodimethylanilines and o-methoxy-p-aminomethylaniline, and the conversion of these compounds into the corresponding 2-methylbenzothiazoles.

The initial o-methoxy- and o-chloro-p-aminodimethylanilines were prepared from the corresponding 2-substituted dimethylanilines via 4-nitro derivatives. 2-Methoxy-4-aminomethylaniline was synthesized by reduction with excess stannous chloride of 2-methoxy-4-nitrophenylmethylnitrosoamine, which, as had been shown previously [5], is formed during the action of excess nitrous acid on 2-methoxydimethylaniline.

3,4-Bis-(dimethylamino)-aniline, which had not been described up to the present time, was prepared by the reduction of 3,4-bis-(dimethylamino)-nitrobenzene, which could be synthesized in a satisfactory yield by heating 2-chloro-5-nitrodimehtylaniline with an alcoholic solution of dimethylamine at 150°.

During the oxidation with potassium dichromate of the p-diamines indicated above in a mixture with sodium thiosulfate in acetic acid solution, the liquid assumed a muddy green color and quickly evolved the corresponding thiosulfonic acids. During the investigation of the compounds obtained the presence of two isomers could not be detected in any case.

The synthesized, substituted p-phenylenediaminethiosulfonic acids were further heated with a mixture of acetic acid and acetic anhydride. However, in contrast to p-aminodimethyl- or diethylaniline-m-thiosulfonic acid [3] the benzothiazole derivatives were formed with small yields and were strongly contaminated with the

corresponding tetraaminodiphenyldisulfides.

In connection with this it seemed necessary to convert the thiosulfonic acids obtained into thiophenols. In accord with the literature data, the reduction of similar thiosulfonic acids usually is carried out with zinc powder in acidic medium [1, 2]. To obtain the benzothiazole derivatives the zinc salts of diaminothiophenols were isolated which were then treated with carboxylic acids, their anhydrides or acid chlorides [2].

However, the preparation of pure zinc salts of diaminothiophenols was rather complicated and involved considerable losses, since it was necessary to separate them by fractional precipitation from zinc sulfide and disulfides.

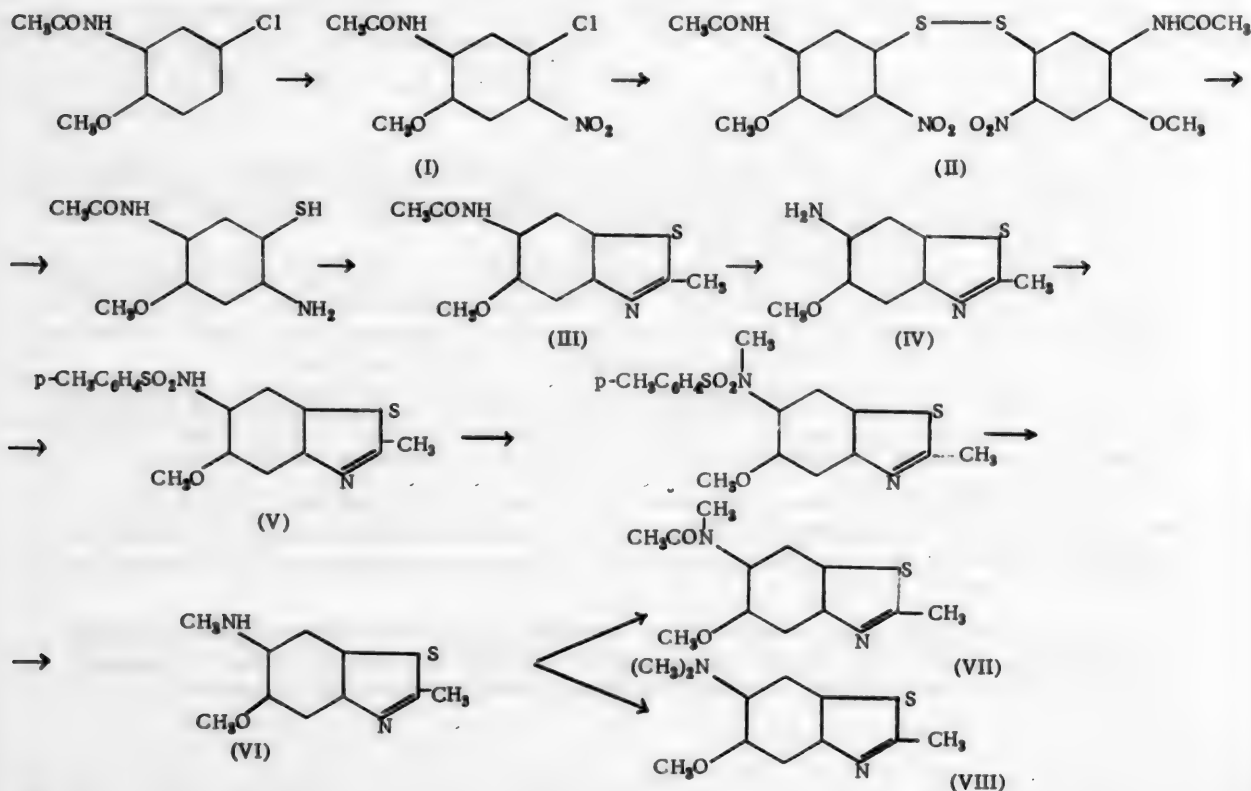
Therefore, taking into account Bemthsen's observations on the formation of p-amino-m-mercaptodimethylaniline during the treatment of the corresponding thiosulfonic acids with ammonium sulfide [6] and the ready closure of the benzothiazole ring by the action of mineral acids on o-acylaminothiophenols [7], we worked out a new method of converting p-phenylenediaminethiosulfonic acids into 6-amino substituted 2-methylbenzothiazoles.

It turned out that such thiosulfonic acids are very readily reduced to diaminothiophenols by sodium sulfide in aqueous or alcoholic solutions. By addition of acetic anhydride to the solution obtained, acetamino derivatives are formed which are smoothly converted into 6-amino substituted 2-methylbenzothiazoles by treatment with hydrochloric acid.

With this method we succeeded in converting all the above-indicated p-phenylenediaminethiosulfonic acids and also the most simple compounds of this series — m-thiosulfonics of p-aminodimethyl- and diethylaniline into derivatives of 2-methylbenzothiazole with excellent yields.

2-Methyl-x(5- or 7)-methoxy-6-dimethylaminobenzothiazole was thereby prepared from 4-amino-2-methoxydimethylaniline-x(3- or 5)-thiosulfonic acid — its picrate had an m.p. of 194-195°; while from the analogous methylaniline derivative 2-methyl-x(5- or 7)-methoxy-6-acetylmethylaminobenzothiazole with an m.p. of 129-130° was synthesized, and by its saponification with 20% hydrochloric acid the 6-methylamino derivative with an m.p. of 77-78° was synthesized. The presence of two isomeric compounds could not be detected by fractional crystallization of the bases and their picrates.

To establish the structure of the above indicated bases and the initial thiosulfonic acids we synthesized, in accordance with the scheme set forth below, 2-methyl-5-methoxy-6-methylamino-6-dimethylamino-, and 6-acetylmethylaminobenzothiazole:



By nitration of 2-methoxy-5-chloroacetanilide in sulfuric acid at 20-25°, only the 4-nitro derivative with an m.p. of 191-192° was obtained, which had already been described, without demonstration of its structure, in several patents [8].

Its structure was established via conversion into the diamine, which gave an intensive indamine reaction and was readily converted by oxidation into the recently described 2-chloro-5-methoxy-1,4-benzoquinone [9, 10].

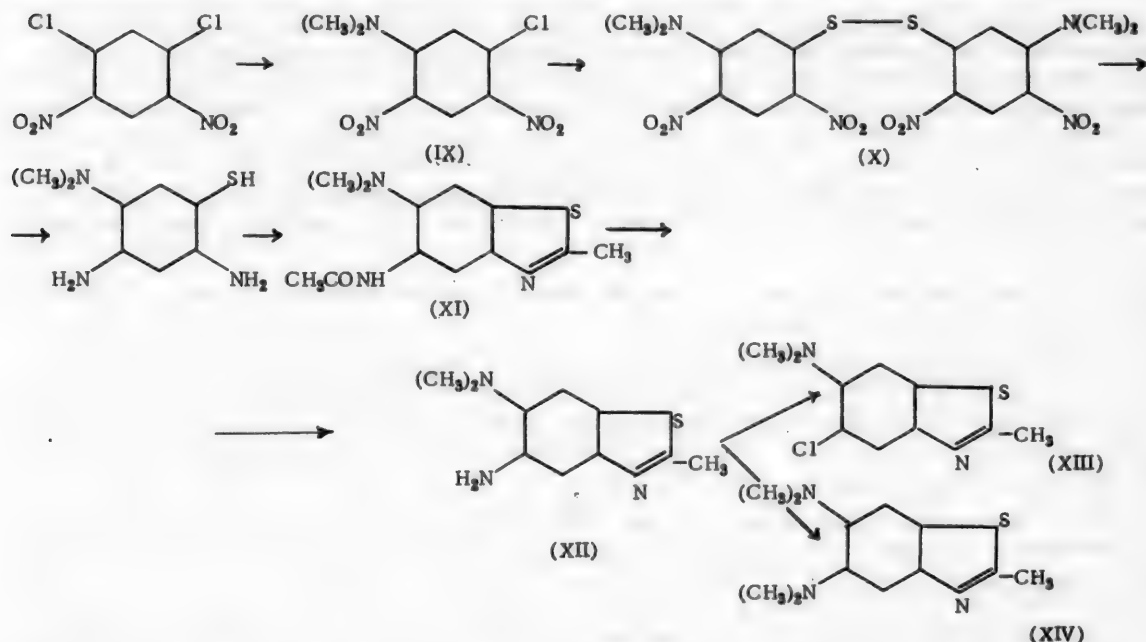
2-Methoxy-4-nitro-5-chloroacetanilide (I) was converted via heating with sodium disulfide into the disulfide (II), which was reduced with zinc powder in acetic acid, and the aminothiophenol salt which was formed was treated with acetic anhydride without isolation; the 2-methyl-5-methoxy-6-acetaminobenzothiazole (III) obtained thereby in excellent yield was saponified with 20% hydrochloric acid, and the amine (IV) was converted by heating with p-toluenesulfochloride in pyridine into the p-tolusulfamino derivative (V).

The latter was then methylated with dimethylsulfate in an aqueous alkali solution and the 2-methyl-5-methoxy-6-methyl-p-tolusulfaminobenzothiazole which precipitated was boiled with hydrochloric acid; 2-methyl-5-methoxy-6-methylaminobenzothiazole (VI) was thereby isolated in the form of colorless crystals with an m.p. 77-78°.

By the acetylation of this compound the acetyl derivative (VII) with an m.p. 129-130° was obtained, while by heating p-toluenesulfonic acid with methyl ether, 2-methyl-5-methoxy-6-dimethylaminobenzothiazole (VIII) was obtained, the picrate of which had m.p. 193-194°.

Compounds VI, VII and VIII were respectively identical with the bases described above obtained from 2-methoxy-4-aminomethyl- and dimethylanilinethiosulfonic acids. Thus, in all these bases the methoxy group is found in position 5 and, consequently the SSO₃H group is located in the para position to the methoxy group in the initial thiosulfonic acids.

2-Methyl-x(5 or 7)-chloro-6-dimethylaminobenzothiazole with m.p. 67-68° was obtained from 2-chloro-4-aminodimethylaniline-x-thiosulfonic acid by reduction with subsequent treatment with acetic anhydride,



while 2-methyl-x(5 or 7)-6-bis-(dimethylamino)-benzothiazole, the picrate of which had a melting point of 170-171°, was respectively obtained from the 2-dimethylamino derivative.

To establish the structure of these compounds we also carried out the synthesis of the corresponding 5-substituted 2-methyl-6-dimethylaminobenzothiazoles (see the scheme above).

4-6-Dinitro-3-dimethylaminobenzene (IX) [11] was converted by the usual method into the disulfide

(X) which was reduced with zinc powder into acetic acid, and the triaminophenol which was formed was treated with acetic anhydride without isolation. The 2-methyl-5-acetamino-6-dimethylaminobenzothiazole (XI), which was thereby obtained in an excellent yield was saponified with 20% hydrochloric acid.

The 2-methyl-5-amino-6-dimethylaminobenzothiazole (XII) which was formed was converted by the Sandmeyer reaction into the 5-chloro derivative (XIII) (colorless crystals with an m.p. 67-68°). The latter proved to be identical with x-chloro-2-methyl-6-dimethylaminobenzothiazole synthesized from 2-chloro-4-amino-dimethylaniline via the thiosulfonic acids.

Upon the methylation of 2-methyl-5-amino-6-dimethylaminobenzothiazole with the methyl ester of p-toluenesulfonic acid in aqueous solution [cf. 2, 3], 2-methyl-5,6-bis-(dimethylamino)benzothiazole (XIV) was obtained in small yield. The picrate of this compound melted at 169-170° and exhibited no melting point depression in a mixed sample with the picrate of x-6-bis-(dimethylamino)-2-methylbenzothiazole, synthesized from 3,4-bis-(dimethylamino)-aniline-x'-thiosulfonic acid, which demonstrated the position of the dimethylamino and thiosulfo groups in the latter compounds.

Thus, during the oxidation of the 2-substituted 4-aminomethyl- and dimethylanilines in the presence of sodium thiosulfate, the thiosulfonic group enters into the para position to the substituent in the 2 position in all cases, and the corresponding 5-thiosulfonic acids are formed, which serve as the starting materials for 5-substituted 2-methyl-6-methyl and dimethylaminobenzothiazoles.

EXPERIMENTAL

(Jointly with A. G. Guseva)

2-Methoxy-4-aminodimethylaniline was prepared by the reduction of 2-methoxy-4-nitrodimethylaniline [5] (4.9 g) with stannous chloride (20.3 g) in hydrochloric acid (20 ml) at 90-95°. The yield was 3.98 g (96%) (from benzene). It consisted of colorless needles, which gradually became rose colored in air, with an m.p. of 91-92° [12].

2-Methoxy-4-aminomethylaniline. a) 5.3 g of 4-nitro-2-methoxyphenylmethyl nitrosamine [5] was gradually introduced into a solution of 40.6 g of stannous chloride in 40 ml of hydrochloric acid (d 1.19). Toward the end of the addition a colorless crystalline precipitate separated out, which dissolved upon dilution with water. The liquid was heated for 30 minutes on a boiling water bath, decolorized by the addition of carbon and filtered. Excess concentrated alkaline solution was added to the filtrate while it was being cooled, the amine which was formed was extracted with ether, the extract was dried with potash, the ether was distilled off, and the residue (a brown-violet crystalline mass) was crystallized from gasoline (200 ml) with added carbon. The yield was 3.4 g (89.4%). It consisted of slightly rose needles with an m.p. of 64-65°. After repeated crystallization from gasoline the m.p. was 67° [13].

b) It was also prepared in a yield of 92.1% of the theoretical by the reduction of 2-methoxy-4-nitromethylaniline with stannous chloride in hydrochloric acid.

2-Chloro-4-aminodimethylaniline was prepared similarly to the preceding compound by the reduction of 2-chloro-4-nitrodimethylaniline [14] (20 g) with stannous chloride (90 g) in hydrochloric acid (120 ml) at 80-90°. After dilution with water and addition of excess 30% sodium hydroxide solution, the amine was isolated in the form of colorless crystals which were filtered off, washed with water and crystallized from 60 ml of gasoline after drying. The yield was 14.72 (86.6%); the m.p. was 62-63° [15].

After a second crystallization from gasoline its melting point did not change. It consisted of colorless flakes, rather stable in air; readily soluble in alcohol and ether, difficultly soluble in gasoline.

Found %: N 16.44, 16.29. $C_8H_{11}N_2Cl$. Calculated %: N 16.42.

2-Chloro-5-nitrodimethylaniline was synthesized by the method specified by van Duin [14]. 15.5 g of 2-chlorodimethylaniline in 100 ml of sulfuric acid (d 1.84) at 10-15° and with stirring was nitrated with a mixture of 6.9 g of nitric acid (d 1.5) and 30 ml of sulfuric acid (d 1.84). The mass was stirred for 2 hours at 15-20°, poured out onto 600 g of ice, and neutralized with aqueous ammonia. The precipitate which settled out was filtered off, washed with water, and after drying was crystallized from 25 ml of ethyl alcohol. The yield was 16.4 g (82%); the m.p. was 62-63° [14]. It consisted of long yellow needles.

1,2-Bis-(dimethylamino)-4-nitrobenzene was prepared by heating 2-chloro-5-nitrodimethylaniline (15 g) with 33% solution of dimethylamine (41 g) and ethyl alcohol (35 ml) in an autoclave at 150° for 10 hours. After

cooling the mass, 700 ml of water was added, the brown precipitate which settled out was filtered off, washed with water, and after drying (weight 12.9-13.2 g) was crystallized from 30 ml of ethyl alcohol. The yield was 11 g (70%); m.p. 59-60°. After two crystallizations from ethyl alcohol it consisted of coarse, orange, rectangular prisms with an m.p. of 62-63°.

Found %: N 19.87, 19.79. $C_{10}H_{15}O_2N_3$. Calculated %: N 20.09.

1,2-Bis-(dimethylamino)-4-aminobenzene was synthesized by the reduction of the preceding compound (10.45 g) with stannous chloride (45 g) in hydrochloric acid (65 ml) at 90°. After heating for 15 minutes on a boiling water bath the liquid was treated with carbon and filtered. The amine was extracted with ether from the almost colorless filtrate after addition of excess concentrated alkali solution. After drying with potash and distilling off the ether, the residue was vacuum distilled.

The yield was 73% of the theoretical; b.p. 130-132° at 9 mm. It consisted of a yellowish oil, which darkened very rapidly in air. It was rather readily soluble in water. In view of the slight stability of the amine, its benzoyl derivative was prepared for analysis. Colorless needles (from ethyl alcohol with an m.p. of 132-133°).

Found %: N 14.96, 14.75. $C_{17}H_{21}ON_3$. Calculated %: N 14.84.

4-Amino-2-methoxydimethylaniline-5-thiosulfonic acid. A solution of 4.9 g of potassium dichromate in 100 ml of 6.5% acetic acid was added over a period of 1 hour at -5° to 0° to a stirred solution of 8.3 g of 2-methoxy-4-aminodimethylaniline and 12.5 g of sodium thiosulfate in 40 ml of 18% acetic acid. After 12 hours the dark green, finely crystalline precipitate which settled out was filtered off and washed with water and acetone, whereupon it became light grey. The yield was 79% of the theoretical. For analysis the preparation was reprecipitated by acetic acid from a 3% soda solution containing sodium sulfide, carefully washed with water and acetone, and dried in a vacuum at 110°. It consisted of almost colorless needles. It was difficultly soluble in water and acetone, rather more readily soluble in ethyl alcohol.

Found %: N 10.12, 10.20. $C_9H_{14}O_4N_2S_2$. Calculated %: N 10.06.

4-Amino-2-methoxymethylaniline-5-thiosulfonic acid was prepared analogously to the preceding compound (in a yield 74% of the theoretical). It consisted of greyish needles. After reprecipitation from soda solution containing sodium sulfite and washing with water and acetone, the preparation obtained was almost colorless.

Found %: N 10.78, 10.71. $C_8H_{12}O_4N_2S_2$. Calculated %: N 10.60.

4-Amino-2-chlorodimethylaniline-5-thiosulfonic acid. 12.5 g of sodium thiosulfate was introduced into a solution of 8.5 g of 2-chloro-4-aminodimethylaniline in 45 ml of 13% acetic acid and then for 1 hour at 0-5° and while the mixture was being stirred, 4.09 g of potassium dichromate in 40 ml of 10% acetic acid was added.

From the solution, which was tinged with a brownish-green color, a grey precipitate of the thiosulfonic acid gradually settled. After 6 hours the product was filtered off and washed with water and acetone. The yield was 8.5 g (60%). Purification of the preparation for analysis was carried out as indicated above. The product consisted of almost colorless needles. It was rather difficultly soluble in water and alcohol and almost insoluble in acetone.

Found %: N 9.83, 9.78. $C_8H_{11}O_3N_2S_2Cl$. Calculated %: N 9.91.

4-Amino-2-dimethylaminodimethylaniline-5-thiosulfonic acid. It was obtained similarly to the preceding compounds by the oxidation at -5 to -7° of 1,2-bis-(dimethylamino)-4-aminobenzene in 20% acetic acid by an acetic acid solution of potassium dichromate in the presence of sodium thiosulfate. The yield of preparation, washed with water and acetone and then reprecipitated from a soda solution, was 68% of the theoretical. It consisted of greyish needles, which hardly changed in air. It was difficultly soluble in water, more readily in ethyl alcohol, and almost insoluble in acetone. For analysis the thiosulfonic acid was additionally crystallized from ethyl alcohol and dried in a vacuum at 100°.

Found %: N 14.51, 14.60. $C_{10}H_{17}O_3N_3S_2$. Calculated %: N 14.42.

2-Methyl-6-dimethylaminobenzothiazole. 7.44 g of 4-aminodimethylanilino-3-thiosulfonic acid [1] was gradually introduced into a solution of 4.2 g of potassium carbonate in 60 ml of water. The mixture was stirred for 10 minutes, and 21.6 g of crystalline sodium sulfide in 30 ml of water was then added to it; a yellow precipitate thereupon settled out, which was rapidly converted into a dark resinous mass. The mixture was heated while being stirred to 75° and the transparent brown solution which formed was cooled to 20°. 3.2 ml of glacial acetic

acid, was poured into the liquid and then 9 ml of acetic anhydride was added during energetic stirring for 2-3 minutes at 20-25°. An oil thereupon settled on the walls of the flask which quickly crystallized. The mixture was stirred for 15 minutes more and acidified with 30 ml of hydrochloric acid (d 1.19). The almost-transparent solution which formed was boiled for 5 minutes, cooled and filtered from the insignificant precipitate.

The latter was washed with 20 ml of water which was combined with the basic filtrate. The liquid was rendered alkaline with 30% sodium hydroxide solution, and the base which separated in the form of an oil was extracted with ether. After drying with potash and distilling off the ether the residue (5.78 g) was vacuum distilled. B.p. 192-194° at 22 mm.

Yield 5.2 g (90%); m.p. 63-64°. After crystallization from gasoline it consisted of colorless prisms with an m.p. of 70-71° [2, 3].

The picrate consisted of shiny, bright yellow flakes (from ethyl alcohol). M.p. 174-176°.

2-Methyl-6-diethylaminobenzothiazole, was prepared analogously to the 4-aminodiethylaniline-3-thiosulfonic acid [1] in a yield of 77.2% of the theoretical. It consisted of a colorless, rapidly-yellowing oil. B.p. 189-190° at 16 mm. (According to Kiprianov and Sych [3], 197-205° at 17 mm).

The picrate consisted of fine yellow prisms (from ethyl alcohol). M.p. 163-165°.

2-Methoxy-4-nitro-5-chloroacetanilide. A mixture of 7.62 ml of nitric acid (d 1.4) and 5.7 ml of sulfuric acid (d 1.84) was gradually added at 20-25° to a solution of 20 g of 2-methoxy-5-chloroacetanilide [16] in 45 ml of sulfuric acid (d 1.84) while the mixture was being stirred. The liquid was stirred for 1 hour at 20-25° and poured out onto 150 g of ice. The precipitate was filtered off, washed with water and dried. The yield was 23.7 g (97%); m.p. 187-188°. It consisted of needles (from ethyl alcohol). M.p. 191-192° [8].

Found %: N 11.27. $C_9H_9O_4N_2Cl$. Calculated %: N 11.45.

2-Methoxy-4-nitro-5-chloroaniline. 2.44 g of 2-methoxy-4-nitro-5-chloroacetanilide was boiled for 1 hour with 75 ml of 25% hydrochloric acid. After filtration the orange solution was diluted with 75 ml of water, and rendered alkaline with soda. The brown precipitate was filtered off, washed with water and dried. The yield was 1.83 g (90%); m.p. 129-130°. It consisted of shiny, dark brown prisms (from alcohol). M.p. 130-131° [8].

Found %: N 13.98. $C_7H_7O_3N_2Cl$. Calculated %: N 13.85.

2-Methoxy-5-chloro-1,4-phenylenediamine. 1.01 g of 2-methoxy-4-nitro-5-chloroaniline was dissolved by heating in 30 ml of 60% ethyl alcohol. After adding 3 ml of acetic acid and 6.5 g of zinc powder the mixture was boiled for 1 hour with a reflux condenser and filtered off from the excess zinc powder. The almost colorless precipitate which fell out on cooling was filtered off and washed with 50% ethyl alcohol. The yield was 0.7 g (81%). After crystallization from benzene it consisted of slightly greyish prisms with an m.p. of 167-168°. It exhibited a clear indamine reaction.

Found %: N 16.32. $C_7H_9ON_2Cl$. Calculated %: N 16.24.

2-Methoxy-5-chloro-1,4-diacetylaminobenzene. A mixture of 0.35 g of 2-methoxy-5-chloro-1,4-phenylenediamine and 1 ml of acetic anhydride was boiled for 15 minutes and the acetic acid was then distilled off and the residue heated for 30 minutes at 250°. After cooling 10 ml of water was added, the precipitate was filtered off, washed with 5 ml of ethyl alcohol and after drying (yield 74% of the theoretical) was twice crystallized from benzene. It consisted of colorless needles with an m.p. of 236-237°.

Found %: N 10.85. $C_{11}H_{13}O_3N_2Cl$. Calculated %: N 10.92.

2-Methoxy-5-chlorobenzoquinone. A solution of 0.22 g of potassium dichromate in 7 ml of water was gradually added to a filtered solution of 0.35 g of 2-methoxy-5-chloro-1,4-phenylenediamine in 10 ml of 10% sulfuric acid at 4-5°. The liquid initially acquired a dark violet, and then a brown color, and a brown precipitate gradually settled out. After 5-6 hours the mass was shaken with ether, the extract dried with sodium sulfate and the ether distilled off. Yellow crystals (0.13 g) with an m.p. of 161-163° were in the residue. After crystallization from benzene yellow prisms with an m.p. of 170-171° [9, 10] were obtained. The substance was readily soluble in ethyl alcohol and ether and difficultly soluble in gasoline.

Found %: Cl 20.37. $C_7H_5O_3Cl$. Calculated %: Cl 20.55.

2,2'-Dinitro-4,4'-dimethoxy-5,5'-diacetylaminodiphenyldisulfide. A solution of sodium disulfide obtained

by heating 9 g of crystalline sodium sulfide with 1.2 g of sulfur was gradually added to a boiling solution of 18.34 g of 2-methoxy-4-nitro-5-chloroacetanilide in 250 ml of ethyl alcohol for 2 hours.

The liquid was then boiled for 6 hours with a reflux condenser, the disulfide precipitate was filtered off and washed with alcohol and water. The yield was 8 g (44%); m.p. 283-284°. It consisted of greenish-yellow leaflets (from gasoline). M.p. 284-285°.

Found %: N 11.79. $C_{18}H_{18}O_3N_4S_2$. Calculated %: N 11.61.

2-Methyl-5-methoxy-6-acetylaminobenzothiazole. A mixture of 7.23 g of 2,2'-dinitro-4,4'-dimethoxy-5,5'-diacetylaminodiphenyldisulfide and 11.7 g of zinc powder was gradually introduced while the mixture was being stirred into 80 ml of glacial acetic acid heated to 90-100°.

After completion of the reduction the mass was heated for 15 minutes on a boiling water bath, and 23 ml of acetic anhydride was then added to it, and the heating was continued on an oil bath at 140-150° for 2 hours. After cooling to 70-80° the liquid was diluted with 50 ml of water, heated to boiling, filtered and the precipitate washed with 50 ml of 50% acetic acid. An excess of a 30% alkali solution was added to the cooled filtrate, combined and washed with acetic acid after dilution with 250 ml of water. The crystalline precipitate which settled out was filtered off, washed with water and dried. The yield was 6.45 g (91%); m.p. 203-205°. After crystallization from ethyl alcohol with added activated carbon the base was obtained in the form of colorless needles with an m.p. of 210-211°.

Found %: N 12.04, 12.08. $C_{11}H_{12}O_2N_2S$. Calculated %: N 11.86.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 199-200°.

2-Methyl-5-methoxy-6-aminobenzothiazole was prepared by boiling 2-methyl-5-methoxy-6-acetylaminobenzothiazole (2 g) with 20% hydrochloric acid (20 ml) for 1 hour. After decolorization with activated carbon the solution was rendered alkaline, the precipitate filtered off, washed with water and dried.

The yield was 90% of the theoretical; m.p. 100-102°. It consisted of colorless prisms (from gasoline). M. p. 104-105° (according to [17] m.p. 106°).

Found %: N 14.51, 14.42. $C_9H_{10}ON_2S$. Calculated %: N 14.43.

The picrate consisted of orange prisms (from alcohol) with an m.p. of 207-208°.

2-Methyl-5-methoxy-6-p-toluenesulfaminobenzothiazole. 3.88 g of the preceding compound, 3.85 g of p-toluenesulfochloride and 16 ml of pyridine were heated for 1 hour on a boiling water bath.

The yellowish solution was diluted with 200 ml of water and neutralized with hydrochloric acid; the precipitate which settled out was filtered off, washed with water and dried. The yield was 98.8% of the theoretical. M.p. 138-139°. After two-fold crystallization from ethyl alcohol it consisted of colorless needles with an m.p. of 147-148°; it was rather readily soluble in ethyl alcohol, and difficultly soluble in gasoline.

Found %: N 7.89. $C_{16}H_{16}O_3N_2S_2$. Calculated %: N 8.05.

The picrate consisted of yellow prisms (from alcohol). M.p. 175-176°.

Found %: N 12.09. $C_{22}H_{19}O_{11}N_5S_2$. Calculated %: N 12.13.

2-Methyl-5-methoxy-6-N-methyl-p-toluenesulfaminobenzothiazole. 1.9 g of dimethylsulfate was added to a filtered solution of 1.75 g of 2-methyl-5-methoxy-6-p-toluenesulfaminobenzothiazole and 0.8 g of sodium hydroxide in 40 ml of water, and the mixture was shaken for 30 minutes. A yellow oil thereupon separated which quickly crystallized. A solution of 0.6 g of sodium hydroxide in 10 ml of water was then added and the mixture was heated for 30 minutes at 70-75°. After cooling the precipitate was filtered off and washed with water. The yield was 1.6 g (88%). The m.p. was 143-145°. It consisted of slightly yellowish prisms (from gasoline). M.p. 148-149°. It was readily soluble in ethyl alcohol and rather difficultly soluble in gasoline.

Found %: N 7.91. $C_{17}H_{18}O_3N_2S_2$. Calculated %: N 7.73.

The picrate consisted of yellow prisms (from alcohol). M.p. 154-155°.

2-Methyl-5-methoxy-6-methylaminobenzothiazole. a) 1.81 g of the preceding compound was boiled for 4 hours with 20 ml of hydrochloric acid (d 1.17). The solution was then diluted with 100 ml of water, rendered

alkaline, and the precipitate which settled out was filtered off and washed with water. The yield was 0.8 g (77%). The m.p. was 73°. After two crystallizations from gasoline it consisted of shiny, yellowish needles with an m.p. of 77-78°. It was very readily soluble in ethyl alcohol and somewhat more difficultly soluble in gasoline.

Found %: N 13.30, 13.42. $C_{10}H_{12}ON_2S$. Calculated %: N 13.46.

The picrate consisted of orange prisms (from alcohol). M.p. 217-218°.

b) 0.5 g of 2-methyl-5-methoxy-6-methylacetylaminobenzothiazole (see below) was boiled for 2 hours with 10 ml of 20% hydrochloric acid. The solution was treated with carbon, rendered alkaline and the base which was formed was extracted with ether. After distilling off the ether the residue weighed 0.37 g (88.9%); m.p. 67-68°. After two-fold crystallization from gasoline the m.p. was 76-77°. It yielded no melting point depression in a mixed sample with the preparation obtained by method (a).

2-Methyl-5-methoxy-6-methylacetylaminobenzothiazole. a) 1.53 g of 4-amino-2-methoxymethylaniline-5-thiosulfonic acid was dissolved at 30-40° in a solution of 0.7 g of potassium carbonate in 5 ml of water, and 2.4 g of crystalline sodium sulfide in 3 ml of water was added to the liquid over a period of 2-3 minutes while it was being stirred. A yellow precipitate thereupon settled out which then almost completely dissolved. After decolorization with activated carbon 14 ml of ethyl alcohol and 1.55 g of acetic anhydride was added to the solution. After 12 hours, the ethyl alcohol and the ethyl acetate were distilled off from the liquid after it had been acidified with hydrochloric acid and the base was liberated by alkalization and extracted with ether. The extract was dried with potash, the ether distilled off and the residue crystallized from gasoline with added carbon. The yield was 3.9 g (87%). It consisted of slightly yellowish prisms with a m.p. of 127-128°.

b) A mixture of 0.1 g of 2-methyl-5-methoxy-6-methylaminobenzothiazole (with an m.p. of 73°) and 0.1 g of acetic anhydride was heated for 2 hours at 115° and after cooling was diluted with 2 ml of water and rendered alkaline with potash. The precipitate which settled out was filtered off and washed with water. The yield was 0.07 g (56%); m.p. 127-128°. A mixed sample of the preparations obtained by both methods melted at 127-128°. After crystallization from gasoline the base was obtained in the form of colorless prisms with an m.p. of 129-130° which did not change during repeated purification. It was rather difficultly soluble in gasoline and readily soluble in ethyl alcohol, ether and acetone.

Found %: N 11.34. $C_{12}H_{14}O_2N_2S$. Calculated %: N 11.20.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 172-173°.

Found %: N 14.76. $C_{18}H_{17}O_3N_3S$. Calculated %: N 14.61.

2-Methyl-5-methoxy-6-dimethylaminobenzothiazole. a) 5.56 g of 2-methoxy-4-aminodimethylaniline-5-thiosulfonic acid was dissolved at 30-40° in a solution of 2.8 g of potassium carbonate in 40 ml of water, and 14.4 g of crystalline sodium sulfide in 20 ml of water was added to the liquid over a period of 2-3 minutes while the mixture was being stirred; a yellow precipitate thereupon settled out which then almost completely dissolved. The liquid was heated to 60°, filtered from the insignificant dark precipitate, and 4.8 ml of glacial acetic acid and, during stirring, 6 ml of acetic anhydride was added to the filtrate after it had been cooled to 15°. An oil thereupon settled out which rapidly crystallized. The mixture was stirred for 15 minutes more, acidified with 20 ml of hydrochloric acid (d 1.17), heated for 30 minutes on a boiling water bath, and then boiled for 5 minutes and filtered from the sulfur and other admixtures. The slightly greenish filtrate was rendered alkaline with a 30% sodium hydroxide solution while being cooled; a greenish oil thereupon settled out which gradually crystallized. The base was extracted with ether, and the ether was distilled off after drying with potash and the residue was heated for 30 minutes in a vacuum on a boiling water bath. The yield was 4.0 g (90%); m.p. 55-57°. After crystallization from gasoline 3.7 g with an m.p. of 58-59° was collected. After a second crystallization from gasoline the melting point of the preparation was raised to 59-60° and it did not change during additional purification. It consisted of colorless prisms; the base was very readily soluble in alcohol, ether and benzene and somewhat more difficultly soluble in gasoline.

Found %: N 12.82, 12.84. $C_{11}H_{14}ON_2S$. Calculated %: N 12.61.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 194-195°.

Found %: N 15.60, 15.68. $C_{17}H_{17}O_3N_3S$. Calculated %: N 15.52.

b) A mixture of 0.21 g of 2-methyl-5-methoxy-6-methylaminobenzothiazole and 0.4 g of the methyl ester of p-toluenesulfonic acid was heated for 15 minutes on a boiling water bath. The thick brownish mass which formed was dissolved in 10 ml of soda, and the solution was filtered off from the insignificant colorless precipitate, which was washed with water and dried.

The weight was 0.08 g; m.p. 73-75°. No melting point depression was displayed in a mixed sample with 2-methyl-5-methoxy-6-methylaminobenzothiazole.

The aqueous solution was shaken with ether and then neutralized with sodium bicarbonate; a yellowish oil was thereupon evolved which was extracted with ether. After drying with potash the ether was distilled off, the residue (0.06 g) entirely crystallized on cooling; m.p. 52-57°. After crystallization from gasoline the product (0.04 g) was converted into the picrate (weight 0.06 g, m.p. 186-190°), which was purified by two-fold crystallization from ethyl alcohol. The weight was 0.03 g; m.p. 193-194°. No melting point depression was displayed in a mixed sample with the picrate of the 2-methyl-5-methoxy-6-dimethylaminobenzothiazole prepared by method (a).

A considerable quantity of quaternary salt was isolated from the aqueous solution after extraction of the base; on heating with ethyl orthoformate in pyridine these salts formed carbocyanine with an absorption maximum at 600 mμ (in alcohol).

4,6-Dinitro-1,3-dichlorobenzene was obtained by the nitration of 1,3-dichlorobenzene (synthesized by the Sandmeyer reaction from m-phenylenediamine [18] or m-chloroaniline [19] with respective yields of 70% and 73% of the theoretical) with a mixture of sulfuric acid and potassium nitrate at ordinary temperatures [20]. The yield of purified product with an m.p. of 101-102° [20] amounted to 65% of the theoretical.

4,6-Dinitro-3-dimethylaminobenzene. A mixture of 23.7 g of 4,6-dinitro-1,3-dichlorobenzene, 13 g of a 33% aqueous solution of dimethylamine, 13 g of crystalline sodium acetate and 230 ml of ethyl alcohol was boiled for 3 hours in a flask with a reflux condenser. After cooling, the precipitate was filtered off and washed with alcohol, water and ether. The yield was 22.2 g (90.5%); m.p. 125°. After crystallization from 300 ml of ethyl alcohol it consisted of shiny yellow needles (19.1 g) with an m.p. of 129° [11].

2,2',4,4'-Tetranitro-5,5'-bis(dimethylamino)diphenyldisulfide. A solution of sodium disulfide obtained by heating 1.3 g of 60% sodium sulfide and 0.5 g of sulfur in 60 ml of alcohol was gradually added over a period of one hour to a boiling solution of 4.91 g of 4,6-dinitro-3-dimethylaminobenzene in 150 ml of ethyl alcohol.

The liquid was then boiled for 30 minutes with a reflux condenser, the yellow precipitate of disulfide which settled out after cooling was filtered off and washed with water and alcohol. The yield was 4.52 g (93%); m.p. 210-212°. For analysis the preparation was crystallized from alcohol, and then from benzene. It consisted of shiny yellow flakes (from benzene). M.p. 216°. It was difficultly soluble in ethyl alcohol and somewhat more readily soluble in benzene.

Found %: N 18.90, 18.94; S 13.45. $C_{16}H_{16}O_8N_6S_2$. Calculated %: N 18.75; S 13.24.

2-Methyl-5-acetyl-amino-6-dimethylaminobenzothiazole. A mixture of 4.84 g of 2,2',4,4'-tetranitro-5,5'-bis(dimethylamino)diphenyldisulfide and 31.1 g of zinc powder was gradually introduced into 50 ml of glacial acetic acid heated to 80-90° and stirred.

After completion of the reduction the thick greyish-white reaction mass was heated for 15 minutes on a boiling water bath, and 6.1 g of acetic anhydride was then added to it and the mixture was boiled for 30 minutes. After cooling to 70-80° the liquid was diluted with 60 ml of water, acidified with hydrochloric acid to an acid reaction as registered by Congo red (45 ml of hydrochloric acid, d 1.18), heated to boiling and filtered from admixtures. The filtrate, while being cooled, was rendered alkaline with a 40% sodium hydroxide solution and shaken with ether. The ether was distilled off from the extract to a volume of 7-10 ml after drying with potash, the precipitate which settled out was filtered off and washed with 2-3 ml of ether. The yield was 3.93 g (76%). It consisted of almost colorless prisms (from gasoline). The m.p. was 123°. It was readily soluble in alcohol and ether, and more difficultly soluble in gasoline.

Found %: N 17.03, 16.88. $C_{12}H_{13}ON_3S$. Calculated %: N 16.86.

The picrate consisted of yellow crystals (from alcohol) with an m.p. 155-156°.

Found %: N 17.44. $C_{13}H_{13}O_3N_3S$. Calculated %: N 17.57.

2-Methyl-5-amino-6-dimethylaminobenzothiazole. 2.49 g of 2-methyl-5-acetyl-amino-6-dimethylaminobenzothiazole was boiled for 2 hours in a flask with a reflux condenser with 7 ml of hydrochloric acid (d 1.19). The almost colorless solution was diluted with 20 ml of water, and after it had been rendered alkaline, was shaken with ether. After drying the extract with potash and distilling off the ether, greyish crystals were left with an m.p. of 88-92°. The yield was 2.05 g (99%).

After crystallization from 30 ml of gasoline 1.33 g with an m.p. of 97-98° was collected. For analysis the preparation was crystallized 2 times more from gasoline. It consisted of yellowish prisms with an m.p. of 100-101°.

Found %: N 20.36, 20.18. $C_{10}H_{13}N_3S$. Calculated %: N 20.08.

The picrate consisted of orange prisms (from alcohol) with an m.p. of 189.5-190°.

Found %: N 19.39. $C_{16}H_{16}O_7N_5S$. Calculated %: N 19.26.

2-Methyl-5-chloro-6-dimethylaminobenzothiazole. a) A solution of 15 g of crystalline sodium sulfide in 15 ml of water was gradually added to a stirred solution of 7.05 g of 4-amino-2-chlorodimethylaniline-5-thiosulfonic acid and 4.25 g of potassium carbonate in 30 ml of water, and the liquid was heated for 10 minutes on a boiling water bath. After separation of an insignificant yellow precipitate, the solution was stirred with 10 ml of ethyl alcohol and 6 ml of acetic anhydride. On the following day the precipitate of sulfur which settled out was filtered off, the filtrate acidified with hydrochloric acid, and after distilling off the alcohol and the ethyl acetate, base was liberated by alkalization and was extracted with ether. After drying with potash and distilling off the ether the residue (3.34 g) was converted into the picrate (yield 6.21 g; m.p. 197-198°), which was crystallized from ethyl alcohol (m.p. after crystallization 200-201°). The base which was evolved by treatment with soda solution was vacuum distilled (b.p. 170-171° at 12 mm). The yield was 2.75 g (40%); m.p. 64-66°. It consisted of almost colorless flakes (from gasoline with a m.p. of 67-68°. The base was readily soluble in ethyl alcohol and ether and somewhat more difficultly soluble in gasoline.

Found %: N 12.20, 12.31. $C_{10}H_{11}N_2SCl$. Calculated %: N 12.36.

b) A solution of 1.03 g of 2-methyl-5-amino-6-dimethylaminobenzothiazole in 12 ml of 10% hydrochloric acid was diazotized at 0° with 0.35 g of sodium nitrite in 2 ml of water. The orange solution of diazonium salt obtained was introduced into a solution of 0.62 g of cuprous chloride and 4 ml of hydrochloric acid (d 1.19), whereupon vigorous evolution of nitrogen occurred. The liquid was diluted with 20 ml of water, filtered from the insignificant precipitate, rendered alkaline, and the base which was evolved was extracted with ether. After distilling off the ether the residue was converted into the picrate, which was crystallized from ethyl alcohol.

The yield was 1.2 g; m.p. 200-201°. 0.3 g of base was isolated by decomposition of the picrate, and after crystallization from gasoline the base melted at 67-68°.

Found %: N 12.41. $C_{10}H_{11}N_2SCl$. Calculated %: N 12.36.

A mixed sample of the bases obtained by both methods and also from the picrates displayed no melting point depression.

The picrate was crystallized from ethyl alcohol for analysis. It consisted of yellow needles with an m.p. of 200-201°.

Found %: N 15.17, 15.19. $C_{16}H_{14}O_7N_5SCl$. Calculated %: N 15.37.

2-Methyl-5,6-bis(dimethylamino)benzothiazole. a) It was obtained analogously to the 5-chloro-6-dimethylamino derivative by the reduction of 4-amino-2-dimethylaminodimethylaniline-5-thiosulfonic acid with sodium sulfide with subsequent treatment of the mercaptide solution obtained with acetic anhydride in the presence of ethyl alcohol and with acidification with hydrochloric acid. The yield of picrate was 75% of the theoretical. The isolated base was purified by vacuum distillation. B.p. 156-157° at 11 mm. It consisted of a yellowish oil which rapidly darkened in air.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 170-171°.

Found %: C 46.56; H 4.52; N 17.90. $C_{17}H_{20}O_7N_6S$. Calculated %: C 46.75, H 4.52, N 18.10.

b) 0.42 g of 2-methyl-5-amino-6-dimethylaminobenzothiazole and 1.12 g of the methyl ester of p-toluenesulfonic acid were heated for 20 minutes on a boiling water bath while being shaken with a solution of 0.32 g of sodium carbonate in 5 ml of water. The slightly turbid yellowish solution was rendered weakly alkaline with soda after filtration and the oil which was evolved was extracted with ether. After drying with potash the ether was driven off and the residue (0.12 g) was converted into the picrate (weight 0.18 g; m.p. 164-168°). It consisted of yellow prisms (from alcohol) with an m.p. of 169-170°. No melting point depression was displayed in a mixed sample with the picrate of the 2-methyl-5,6-bis(dimethylamino)benzothiazole obtained by method (a).

SUMMARY

1. The oxidation by potassium dichromate of a number of 2-substituted 4-aminomethyl- and dimethyl-anilines in the presence of sodium thiosulfate was investigated. It was shown that the corresponding 5-thiosulfonic acids are thereby smoothly obtained.

2. A new general method of converting p-phenylenediaminethiosulfonic acids into 6-amino derivatives of 2-methylbenzothiazole was worked out.

3. The synthesis of a number of 5-substituted 6-dimethylamino-2-methylbenzothiazoles and also of the corresponding 6-amino- and 6-methylamino-5-methoxy derivatives was carried out.

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* See Consultants Bureau Translation, page 1217.

** See Consultants Bureau Translation, page 307 and 313 ff.



INVESTIGATION OF THE REDUCTION OF γ -DINITRILES

BY VYSHNEGRADSKY'S METHOD

A. P. Terentyev and V. G. Yashunsky

The reduction of nitriles by Vyshnegradsky's method with sodium in alcohol under various conditions can be successfully used for the synthesis of several difficultly-obtainable cyclic nitrogenous bases [1, 2, 3, 4].

Cyclization can occur in the case of reduction of nitriles on which, along with the nitrile group, there is another nitrile group, a primary amine group or a keto group, as a rule in the β - or γ -position.

The formation of cyclic imines during the reduction of nitriles by succinic and glutaric acids was detected for the first time by Ladenburg [5], who, however, did not establish the quantitative ratios between the linear and cyclic products thereby obtained. The formation of ammonia and volatile bases was also observed by other authors during the reduction of 1,2- and 1,3-dinitriles [6, 7].

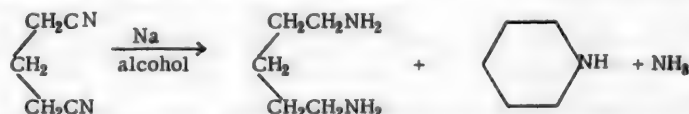
Korshak and Rafikov [8] found that during the reduction of nitrile by adipic acid, a small quantity of α -ethylpyrrolidine was formed along with the hexamethylenediamine.

In spite of the large amount of data concerning the formation of cyclic imines during the reduction of nitriles by sodium in alcohol, up to the present time no systematic study of the conditions and factors which influence the cyclization process or the mechanism of this reaction has been carried out. Apparently, this is due to the difficulty of separating and determining amines under these conditions.

We undertook a detailed study of this reaction in the simplest example — the nitrile of glutaric acid, using the analytical method of investigating the end products without isolating them.

About 1 g (approximately 0.01 mole) of the dinitrile and 3.2 g of metallic sodium were taken for each experiment. Thus, in all the experiments approximately one mole of hydrogen, formed due to the reaction of sodium with alcohol, was available per mole of nitrile.

The reduction of glutaronitrile leads to the following products:



In addition, some ammonia can be formed due to the partial saponification of the nitrile.

Secondary linear amines ($\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}-(\text{CH}_2)_6-\text{NH}_2$) are practically not formed under these conditions.

The method of analysis, worked out on the basis of the work of Mizuch and Isavchenko [9], consisted of the determination of ammonia via its precipitation in the form of the complex with sodium cobaltinitrite, while penta-methylenediamine was precipitated with the aid of the nitrite method of Van Slyke in a modified Ioanisani [10] microdetermination apparatus. The quantity of piperidine was found as the difference between the total amine nitrogen determined by titration of the reaction products and the nitrogen of the diamine and ammonia. The method was verified on several artificial mixtures of these three components and manifested a precision to $\pm 0.5\%$.

The experiment (No. 1) involving the reduction of the nitrile of glutaric acid with sodium in absolute ethyl alcohol at a molar ratio of the reacting components nitrile : alcohol : sodium = 1:95:15 was taken as the standard for comparison. The total yield of diamine and piperidine amounted to 77% (calculating on the basis of nitrile taken) under these conditions, while the molar ratio of the first and second was equal to 4:1.

It was found that the duration of the reaction appreciably influenced the yields of linear and cyclic amines: the slower the reaction proceeded, the greater the extent to which piperidine was formed. The quantity of diamine obtained was also thereby increased; however, very prolonged reduction lowered its yield. Thus, the

time of reaction is a dependent variable and can be regulated by the reaction temperature, the method of introducing sodium and the quantity of alcohol, while the determining factor here, apparently, is the rate of solution of sodium in alcohol, i.e., the intensity of hydrogen formation.

Our experiments showed that a less energetically proceeding reaction of sodium with alcohol facilitates cyclization under the given conditions. Therefore, the increase in the quantity of alcohol for reduction, which accelerates the solution of the sodium, leads to diminished yields of diamine, and particularly of piperidine (Fig. 1).

Diminished nitrile concentration due to addition of inert solvents to the alcohol, as one would expect, favorably influences the course of cyclization and negatively influences the formation of diamine; the total yield of both amines remains almost the same (Fig. 2).

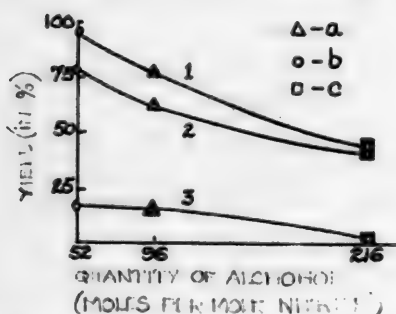


Fig. 1. The yield of reaction products as a function of the quantity of alcohol. 1) Total yield; 2) yield of diamine; 3) yield of piperidine. Experiment numbers: a) 1; b) 3; c) 4.

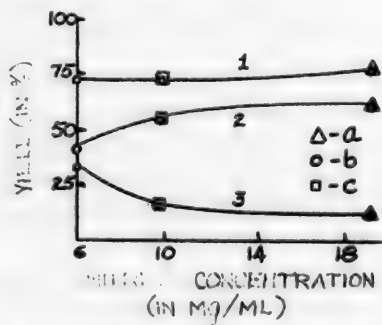


Fig. 2. Yield of reaction products as a function of the nitrile concentration. 1) Total yield; 2) yield of diamine; 3) yield of piperidine. Experiment numbers: a) 1; b) 8; c) 9.

The addition to the reaction mixture of nickel formate (0.3 g) which was reduced to metallic nickel, almost tripled the ratio of linear and cyclic reaction products in the direction of diamine - 11:1 (in the standard experiment it was equal to 4:1). Apparently in the presence of this catalyst a portion of the uselessly evolved molecular hydrogen also participates in the reduction of the nitrile.

The use of an alloy of sodium with potassium (2% K) for the reduction, as one should expect [11], increased the yield of both products; the total amine yield reached 93%, calculated on the basis of the nitrile.

The reduction was carried out with finely divided sodium with the object of elucidating the influence of the metal surface on the course of the reaction; there was no substantial difference in the results in comparison with the standard conditions.

Treatment of the nitrile in alcohol with alcoholate prior to the reduction was reflected only in an increase of the diamine yield to 80%, calculated on the basis of nitrile.

Interesting data were obtained by the reduction of glutaric nitrile in other alcohols - methyl, butyl and cyclohexyl (Table 1, about 50 ml of alcohol was taken in all experiments). An increase in the yields of diamine and piperidine was detected from methyl alcohol to ethyl and butyl alcohols. As a result of the reduction of nitrile in cyclohexyl alcohol it was shown that piperidine is formed in twice as large a quantity as the diamine with a total amine yield of 91%. In the given case, apparently, the high reaction temperature (165°) plays a decisive role.

Thus, as a result of the study of the reduction of glutaric nitrile by sodium in alcohol, it was established that increasing the duration of the reaction, decreasing the nitrile concentration, and increasing the reaction temperature facilitate the course of the cyclization process with formation of piperidine.

In order to elucidate the influence of substituents in the α -position of glutaric nitrile on the degree of formation of cyclic products in this reaction, we carried out the reduction of the dinitriles of α -methyl and α -phenylglutaric acids under standard conditions. It was found that both substituted nitriles give much higher yields of cyclic imines (Table 2).

With the object of studying the cyclization mechanism during the reduction of dinitriles by the Vyshnegradsky method, we treated pentamethylenediamine with sodium in alcohol under standard conditions. The formation of appreciable quantities of ammonia was not detected under these conditions. Our results confirmed the previously

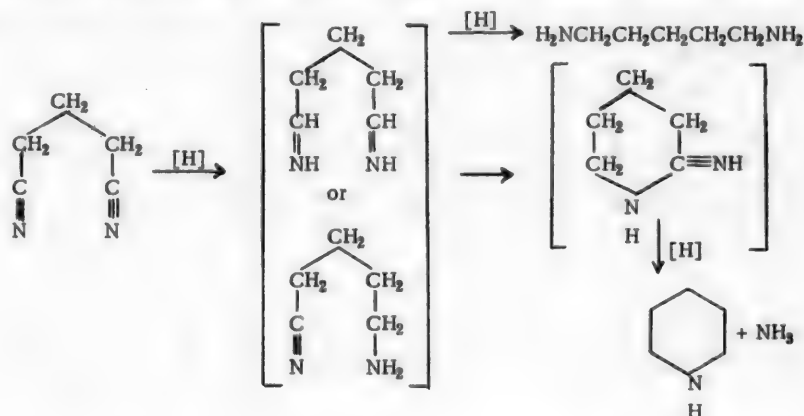
TABLE 1
Reduction of Glutaric Acid Nitrile in Various Alcohols

Expt. No.	Alcohol				Ratio diamine piperidine
		Diamine	Piperidine	Total	
12	Methyl	27.0	9.0	36.0	3/1
1	Ethyl	61.5	15.5	77.0	4/1
13	n-Butyl	80.0	18.5	98.5	4.3/1
14	Cyclohexyl	30.0	61.0	91.0	1/2

TABLE 2
Reduction of Dinitriles of Glutaric Acids in Ethyl Alcohol

Expt. No.	Acid Nitriles	Yield of products (in moles %)			Ratio A/B	Yield of products according to the literature data.		
		Diamine (A)	Cyclic product (B)	Total		Diamine	Cyclic product	Reference
1	Glutaric	61.5	15.5	77.0	4/1	80**	—	[5]
15	α -Methylglutaric	68.5	21.0	89.5	3/1	47	23	[7]
16	α -Phenylglutaric	34.5*	34.0	68.5	1/1	—	59***	[1]

(amidine), which is readily converted by the action of sodium in alcohol [12] into piperidine with the evolution of ammonia



Apparently the slowest of these reactions is the direct cyclization — the establishment of the C-N bond. Consequently increased duration and increased temperature favor its passage

Decreased nitrile concentration also exerts a positive influence on the formation of piperidine, slowing the hydrogenation of the intermediate products to diamine.

If our hypothesis concerning the mechanism of cyclization is correct, then one can expect that the mechanism of the reduction of nitriles by Vyshnegradsky's reaction is in general the same as during their catalytic hydrogenation [13], i.e., the intermediate stage appears to be an imine.

EXPERIMENTAL

The dinitrile of glutaric acid was prepared from 1,3-dibromopropane [14], b.p. 110-112° at 3 mm, n_D^{25} 1.4330, d_4^{25} 0.9825, MR_D 24.89, calculated 24.93, the literature data: b.p. 131-134° at 10 mm [14].

The dinitrile of α -methylglutaric acid was prepared by an analogous method from 1,3-dibromobutane b.p. 137-138° at 14 mm, n_D^{25} 1.4320; d_4^{25} 0.9512; MR_D 29.49, calculated 29.55. Literature data: b.p. 134°

* The low yield of diamine is apparently to be explained by the fact that it could not be entirely distilled off from the reaction products.

** The yield is given for the hydrochloride.

*** The reduction was carried out in butyl alcohol.

proposed hypothesis [5] concerning the possibility of the formation of piperidine in this reaction due to the cleavage of ammonia from the diamine. It could therefore be expected that the process of the reduction of glutaric acid nitrile by sodium in alcohol proceeds according to the following scheme (just as was established in the case of the catalytic hydrogenation [12]): first stage — formation of intermediate diamine or amino-nitrile, then either further hydrogenation to diamine or cyclization into piperidinimine

TABLE 3
Reduction of Glutaric Acid Dinitrile

Expt. No.	Alcohol	Reaction conditions	Nitrile (in g)	Dura- tion (min)	N found (in mg)			Obtained (moles)			Yield (mole %)		Ratio diam- ine:piperid- ine (moles)
					in dis- tillate	of di- amine	of am- monia	of pip- eridine	of nitrile	di- amine	piper- idine	total	
1	Ethyl 50 ml	Add. of nitrile sol. to Na, heating	0.950	15	274	174	78	0.00622	0.00157	0.01010	61.5	15.5	4:1
2	Ethyl 50 ml	Intro. of Na to nitrile sol. heating	0.896	22	253	171	51	0.00630	0.00186	0.00953	66.0	19.5	3.4:1
3	Ethyl 30 ml	As in Experiment 1	0.940	28	262	220	19	0.00786	0.00164	0.01000	78.5	16.5	5:1
4	Ethyl 120 ml	As in Experiment 1	0.911	6	267	113	151	0.00403	0.00021	0.00970	41.5	2.0	20:1
5	Ethyl 50 ml	Cooling to 20°	0.898	60	262	95	125	0.00339	0.00300	0.00954	35.5	31.5	1:1
6	Ethyl 50 ml	As in Expt. 1. Add. of 0.3 g of nickel formate	0.940	18	273	183	82	0.00654	0.00057	0.01000	65.5	6.0	11:1
7	Ethyl 50 ml	Addition of thenitrile solution to an alloy of Na and K (K 0.07 g), heating	0.962	28	280	208	43	0.00743	0.00207	0.01020	73.0	20.0	3.5:1
8	Ethyl 50 ml; toluene 100 ml	As in Experiment 1	0.898	7	261	111	108	0.00396	0.00300	0.00954	41.5	31.5	1.3:1
9	Ethyl 50 ml; dioxane 50 ml	As in Experiment 1	0.968	13	274	160	89	0.00572	0.00179	0.01030	55.5	17.5	3:1
10	Ethyl 50 ml	As in Experiment 2; heating for 10 minutes with 1.4 g NaOC ₂ H ₅ before the reaction	0.907	23	256	217	20	0.00775	0.00136	0.00965	80.0	14.0	5.7:1
11	Ethyl 50 ml; toluene 15 ml	Addition of the nitrile solution to finely divided Na while the mixture was being stirred	0.902	6	258	144	92	0.00515	0.00157	0.00960	54.0	16.0	3.4:1
12	Methyl 50 ml	As in Experiment 1; Tempera- ture 70°	0.892	7	258	72	174	0.00257	0.00086	0.00950	27.0	9.0	3:1
13	n-butyl 50 ml	As in Experiment 2; Tempera- ture 120°	0.947	40	260	226	8	0.00807	0.00186	0.01010	80.0	18.5	4.3:1
14	Cyclohexyl 50	As in Experiment 2; Tempera- ture 165°	0.913	35	218	82	53	0.00294	0.00592	0.00970	30.0	61.0	1:2
Reduction of α -substituted glutaric acid dinitriles													
15	α -Methylglutaro- nitrile; ethyl 50 ml	As in Experiment 1	1.084	16	266	192	45	0.00685	0.00207	0.01000	68.5	21.0	3:1
16	α -Phenylglutaro- nitrile; ethyl 50 ml	As in Experiment 1	1.648	17	240	94	100	0.00336	0.00328	0.00968	34.5	34.0	1:1

at 13 mm [7].

The dinitrile of α -phenylglutaric acid was synthesized from benzyl cyanide and acrylonitrile [1], b.p. 155-156° at 3 mm, n_D^{20} 1.5250. Literature data: b.p. 181-183° at 8.5 mm, n_D^{25} 1.5237 [1].

Pentamethylenediamine was prepared by the reduction of the dinitrile of glutaric acid by sodium in butyl alcohol, b.p. 178-179.5°. Literature data: b.p. 178-180° [15].

Reduction of Glutaric Acid Nitrile in Ethyl Alcohol (Standard Experiment No. 1)

3.2 g of metallic sodium was placed in a 100 ml three-necked flask supplied with a dropping funnel and a reflux condenser to which was joined a Tishchenko flask with 10 ml of 0.25 N HCl. A solution of 0.950 g (0.0101 mole) of glutaric acid nitrile in 50 ml of absolute ethyl alcohol was rapidly added from a dropping funnel. The flask was heated on a boiling water bath. After all the sodium had reacted (15 minutes), 30 ml of water was poured in.

After cooling, the mixture was transferred to a round-bottom flask with a long neck and, after it had been supplied with a Kjeldahl drop trap, the alkaline solution was subjected to distillation with steam heated to 150°. The distillate was collected in a flask with 74.7 ml of 0.25 N HCl (the end of the adapter was placed below the surface of the liquid in the receiving flask). The end of the distillation was determined by the absence of an alkaline reaction with litmus (about 3 hours). The contents of the Tishchenko flask were then poured off into the distillate and the excess acid in it was titrated with alkali with methyl red as the indicator. 15.9 ml of 0.1 N NaOH was consumed in the titration. The titrated solution was acidified and concentrated on a water bath to a volume of about 30 ml and transferred to a 50 ml measuring flask. 3 ml of a 10% sodium acetate solution and 10 ml of dioxane were added to 10 ml of the solution from the measuring flask. A cooled solution of 1.5 g of the binary salt of sodium cobaltinitrite in 25 ml of water was also added to the cooled mixture. After standing for 15 minutes in the cold the mixture was filtered through a No. 4 glass filter. The precipitate - a bright yellow powder - was washed with 20 ml of dioxane. The filtrate was transferred into a 100 ml measuring flask.

The primary amine group content in one milliliter of this solution was determined by Van Slyke's method. This was carried out in an apparatus of Ioanisiani [10] design for the microdetermination of deamination and the absorption of nitrogen oxides was carried out in a glass medical syringe joined with a gas microburette. The syringe was shaken for 8 minutes, and the pentamethylene was completely determined after 20 minutes.

0.306 ml N_2 (18°, 734 mm) 0.310 ml N_2 (19°, 734 mm). In 1 ml of solution, found mg N: 0.3476, 0.350, average 0.348 mg.

The precipitate from the filter (ammoniacal complex) was decomposed with alkali, with the ammonia being distilled off into titrated acid. The quantity of ammonia was found by reversible titration (4.46 ml of 0.25 N HCl) to be 0.001115 g-equiv, which corresponded to 15.6 mg N.

Thus, in the reaction mixture was found:

total content of ammonia and ammine nitrogen 0.01959 g-equiv., or 274 mg N; ammonia nitrogen 15.6 mg X 5 = 78 mg; pentamethylenediamine nitrogen 0.348 mg X 500 = 174 mg N, hence piperidine nitrogen = 22 mg

The complete experimental data are set forth in Table 3.

The subsequent experiments were carried out by analogous methods. Only in the experiments with butyl and cyclohexyl alcohols, and also with toluene, 0.25 N H_2SO_4 was used to titrate the steam distillate, and the steam distillate was twice treated with the acid solution, after which the bases were determined by titration.

SUMMARY

1. The conditions and factors which influence the cyclization processes which are accompanied by the formation of piperidine were studied in the case of the reduction of glutaric acid dinitrile with sodium in alcohol.

2. It was found that the dinitriles of α -methyl- and α -phenylglutaric acids give in this reaction larger yields of cyclic products than the unsubstituted dinitrile.

3. A hypothesis concerning the reaction mechanism of the cyclization of dinitriles during reduction by Vyshnegradsky's method is proposed.

4. A method was worked out for determining pentamethylenediamine, piperidine, and ammonia in mixtures.

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CONVERSION OF HYDROAROMATIC ALDEHYDES AND KETONES INTO AROMATIC HYDROCARBONS BY DEHYDRATION

A. A. Petrov and N. P. Sopov

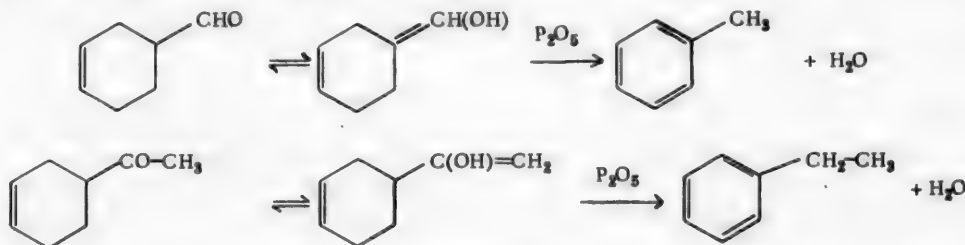
The authors of this paper have shown in their preceding works that hydroaromatic alcohols containing two double bonds in the ring and a hydroxyl group in the side chain on the carbon atom adjacent to the ring are capable of being converted into aromatic hydrocarbons [1,2], by the action of dehydrating agents. The use of dehydrating catalysts with a milder action permits one to obtain in certain cases vinylcyclohexadiene hydrocarbons as intermediate products, which correspond in structure with the initial alcohol. These hydrocarbons are readily isomerized into aromatic hydrocarbons by the action of acids. Thus, it was shown that the reaction proceeds via a stage of formation of nonbenzenic hydrocarbons, and the isomerization appears to be a process which occurs subsequent to the dehydration.

In the light of these data it is of undoubted interest to investigate in the field of dehydration of other substances with two double bonds and oxygen atoms in the side chain in the α -position to the ring. As such subjects of investigation, we chose unsaturated hydroaromatic aldehydes and ketones — products of the condensation of diene hydrocarbons and their derivatives with α , β -unsaturated aldehydes and ketones of the aliphatic series. These substances, taking into account the possibility of their existence in enolic forms, can be considered as dienic hydroaromatic alcohols, and, consequently, one can expect the formation of hydroaromatic compounds upon their dehydration.

No such isomerization has been described in the literature. However, several cases of the formation of aromatic hydrocarbons upon the heating with concentrated hydrobromic acid or zinc chloride of unsaturated hydroaromatic ketones with a double bond and a carbonyl group in the nucleus are well known [3, 4].

The compounds which we investigated did not split off water during heating with concentrated HBr. They underwent cracking on distillation with ZnCl_2 . However, under other conditions, specifically during distillation with P_2O_5 , they yielded aromatic compounds with the same number of carbon atoms. In the case of ketones, the aromatic compounds were also obtained during contact with active Al_2O_3 at 350–400°.

Thus, from Δ^3 -tetrahydrobenzoic aldehyde, toluene was obtained; from Δ^3 -tetrahydroacetophenone, ethylbenzene; from the homologous primary and secondary substances, the corresponding homologs of toluene and ethylbenzene, and, finally, from p-chlorotetrahydroacetophenone, p-chloroethylbenzene. The reaction can be depicted in the following manner for the two simplest cases:



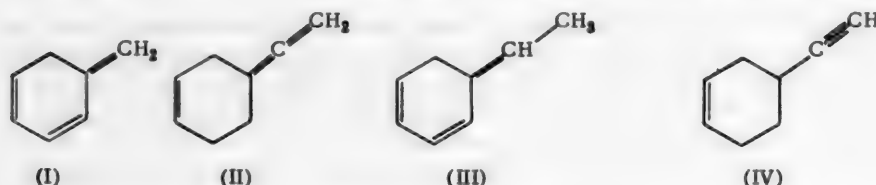
The yield of aromatic compounds amounted to 10–35% from aldehydes and 30–35% from ketones. Thus, hydroaromatic ketones yielded significantly better results. In the case of aldehydes the greater portion of the initial substance was lost as a consequence of polymerization under the influence of P_2O_5 .

The condensation product of cyclopentadiene with methylvinylketone — 1-acetyl-2,5-endomethylene-cyclohexene-3 — was entirely resinified by distillation over P_2O_5 , and we did not succeed in obtaining an aromatic hydrocarbon from it.

The condensation product of cyclohexadiene with methylvinyl ketone - 1-acetyl-2,5-endoethylenecyclohexene-3 - yielded a mixture of aromatic hydrocarbons in insignificant yields. By oxidizing this mixture with nitric acid, a high melting acid was obtained, the methyl ester of which melted at 129°. It is possible that this was contaminated with the dimethyl ester of terephthalic acid. This substance was not studied in greater detail.

The aromatic compounds obtained as a result of the dehydration of all the other aldehydes and ketones had constants close to those given in the literature, and during oxidation with nitric acid yielded aromatic acids, corresponding to them in structure, in a sufficiently pure state.

We can only draw certain preliminary conclusions relative to the mechanism of the described reaction. Probably the enol forms of hydroaromatic aldehydes and ketones participate in the reaction. In the case of aldehydes, the initial reaction products can only be a hydrocarbon with a semicyclic double bond (I), which, in acid medium, must rapidly rearrange into an aromatic hydrocarbon. The isomerization of the hydrocarbons of the semibenzenic series into aromatic hydrocarbons in the presence of acids proceeds readily, even if there are two alkyl groups on a given carbon atom of the ring: migration of the alkyl occurs [5,6]. In the case of hydroaromatic ketones, dehydration can lead to the formation either of an additional hydrocarbon with a semicyclic double bond (II) or (III), or the corresponding acetylenic hydrocarbon (IV). Ready conversion into aromatic hydrocarbons in the presence of dehydration catalysts is possible for all these substances. Isomerization of acetylenic hydrocarbons was not investigated directly; however, it is well known that during the dehydration, for example, of 1-acetylenylcyclohexanol-1, the formation of ethylbenzene is observed [7,8, 9]:



The reaction described here of hydroaromatic aldehydes and ketones, at least in the case of ketones, is of considerable interest as a new route of conversion of diene compounds into aromatic compounds, avoiding the stage of dehydrogenation of the ring, and without there being any conversion due to the carbonyl group, which is usually employed in these cases [10].

On the other hand, this reaction permits new ways of determining the structure of homocyclization products with the participation of dienic compounds and α,β -unsaturated aldehydes and ketones, since it can be employed when other methods do not permit the reliable determination of the position of the substituent (for example, for the determination of the position of the halogen in the condensation products of β -halogenodienes with α,β -unsaturated aldehydes and ketones).

EXPERIMENTAL

The preparation of the majority of the starting hydroaromatic aldehydes and ketones by the condensation of dienic hydrocarbons and their derivatives with the corresponding α,β -unsaturated aldehydes and ketones has been described in the preceding communications [11,12,13].

The reaction with P_2O_5 was carried out under the following conditions: The substance (about 10-20 g) was stirred in a distilling flask while being cooled with water with a one-and-a-half excess of P_2O_5 . The energetic reaction began quickly (in the case of several ketones, a small amount of heating was required). The mixture was then gradually heated on a metallic bath to 300°. The reaction products were collected by joining to the flask a condenser with a small receiving flask. After washing with 80% H_2SO_4 (to eliminate the unreacted starting materials), they were distilled at ordinary pressure.

The aromatic compounds obtained were oxidized by heating for several hours at 100-120° with a two-three-fold excess of 25% nitric acid in sealed glass tubes. The acids settled out on cooling the tubes, and were additionally extracted with ether and recrystallized from water. During the oxidation, the formation of small quantities of nitrocompounds was observed.

Terephthalic acid was converted, by heating with methyl alcohol and concentrated H_2SO_4 in sealed tubes for 6 hours at 100-120°, into the dimethyl ester. The latter was recrystallized from methyl alcohol.

o-Phthalic acid was converted, by heating with acetic anhydride, into the anhydride. The acetic anhydride was evaporated off in a vacuum.

The experimental data for the separate aldehydes and ketones are set forth below.

1. Δ^3 -Tetrahydrobenzoic aldehyde (b.p. 58-59° at 18 mm, n_D^{20} 1.4739) yielded on distillation over P_2O_5 toluene with a yield of about 10%:

B.p. 109-110°, d_4^{20} 0.8623, n_D^{20} 1.4939.

Literature data [14]: b.p. 110.6°, d_4^{20} 0.8670, n_D^{20} 1.4969.

By oxidizing the substance, benzoic acid with a m.p. of 120° [15] was obtained.

2. 6-Methyl- Δ^3 -tetrahydrobenzoic aldehyde (b.p. 70-72° at 18 mm, n_D^{20} 1.4678) yielded o-xylol (12%) under the same conditions:

B.p. 142-144°, d_4^{20} 0.8808, n_D^{20} 1.5050.

Literature data [14]: b.p. 144.4°, d_4^{20} 0.8802, n_D^{20} 1.5055.

Oxidation yielded o-phthalic acid with a m.p. of 187-188°; the anhydride had a m.p. of 130.5° [15].

3. 4-Methyl- Δ^3 -tetrahydrobenzoic aldehyde (b.p. 73-75° at 18 mm, n_D^{20} 1.4732) yielded p-xylol (10%):

B.p. 136-138° at 750 mm, d_4^{20} 0.8642, n_D^{20} 1.4956.

Literature data [14]: b.p. 138.4°, d_4^{20} 0.8611, n_D^{20} 1.4958.

Terephthalic acid was obtained by oxidation of the substance. The dimethyl ester melted at 140°.

4. 2,6-Dimethyl- Δ^3 -tetrahydrobenzoic aldehyde (b.p. 80-82° at 18 mm, n_D^{20} 1.4678) yielded 1,2,3-trimethylbenzene (15%):

B.p. 172-174° at 747 mm, d_4^{20} 0.8879, n_D^{20} 1.5108.

Literature data [14]: b.p. 176°, d_4^{20} 0.8944, n_D^{20} 1.5139.

Hemimellitic acid with a m.p. of 190° (from water) was obtained by oxidation. The trimethyl ester melted at 100-102°.

5. 2,4,5-Trimethyl- Δ^3 -tetrahydrobenzoic aldehyde was prepared from dimethylbutadiene and crotonaldehyde by heating for 8 hours at 120° in sealed glass tubes:

B.p. 96.5-97.5 at 18 mm, d_4^{20} 0.9274, n_D^{20} 1.4759, MR_D 46.29, calculated 45.72.

0.1400 g substance: 0.4047 g CO_2 ; 0.1436 g H_2O . Found %: C 78.88; H 10.27. $C_{10}H_{14}O$. Calculated %: C 78.90; H 10.6.

On distilling with P_2O_5 , 2,4,5-trimethyl- Δ^3 -tetrahydrobenzoic aldehyde yielded 1,2,4,5-tetramethylbenzene (durene) with a m.p. of 79° in a yield of 15%, which was in agreement with the literature data [14,15].

9.43 g substance: 29.97 mg CO_2 ; 9.18 mg H_2O . Found %: C 89.90; H 10.89. $C_{10}H_{14}$. Calculated %: C 89.49; H 10.56.

The molecular compound of the substance with 1,3,5-trinitrobenzene had a m.p. of 96-98°, which also corresponded to the literature data for durene [15].

6. Δ^3 -Tetrahydroacetophenone (b.p. 77-79° at 18 mm, n_D^{20} 1.4698) yielded ethylbenzene in a yield of 35% on distillation with P_2O_5 .

B.p. 134-135° at 748 mm, d_4^{20} 0.8642, n_D^{20} 1.4958.

On distilling the same substance with Al_2O_3 at 350-400°, ethylbenzene was obtained with a b.p. of 134-136°, d_4^{20} 0.8622, n_D^{20} 1.4935. Yield 35%.

Literature data [14]: b.p. 136.2°, d_4^{20} 0.8670, n_D^{20} 1.4959.

Benzoic acid with a m.p. of 119-120° (for both samples) was obtained by oxidation.

7. 2-Methyl- Δ^3 -tetrahydroacetophenone (b.p. 85-86° at 18 mm, n_D^{20} 1.4682) yielded o-methylethylbenzene with a yield of 32% on distillation with P_2O_5 :

B.p. 163-165 at 752 mm, d_4^{20} 0.8807, n_D^{20} 1.5006.

Literature data [14]: b.p. 165.2°, d_4^{20} 0.8807, n_D^{20} 1.5046.

o-Phthalic acid with a m.p. of 184-185° was obtained by oxidation. The anhydride had a m.p. of 130.5°.

8. 4-Methyl- Δ^3 -tetrahydroacetophenone (b.p. 91-92° at 18 mm, n_D^{20} 1.4720) yielded p-methyl-ethylbenzene (35%) with the aid of P_2O_5 :

B.p. 161-162 at 756 mm, d_4^{20} 0.8608, n_D^{20} 1.4955.

Literature data [14]: b.p. 162°, d_4^{20} 0.8612, n_D^{20} 1.4950.

Terephthalic acid was obtained by oxidation of the substance. The dimethyl ester had a m.p. of 140°.

p-Methylethylbenzene with a b.p. of 159-162°, d_4^{20} 0.8632, n_D^{20} 1.4958, was obtained by passing the substance over Al_2O_3 at 350-400°.

The results of oxidation were the same as in the preceding case.

9. 4-Chloro- Δ^3 -tetrahydroacetophenone (b.p. 120-121° at 18 mm, n_D^{20} 1.4972) yielded p-chloro-ethylbenzene with a yield of 40%:

B.p. 178-182°, d_4^{20} 1.0290, n_D^{20} 1.5185.

0.1584 g substance: 0.1588 g AgCl. Found %: Cl 24.80. C_8H_7Cl . Calculated %: Cl 25.22.

The literature data for p-chloroethylbenzene: b.p. 179-180°, d_4^{20} 1.0575, n_D^{20} 1.5223.

Thus, the substance obtained by us was not entirely pure. However, upon oxidation it yielded the expected p-chlorobenzoic acid with a m.p. of 240°.

10. 1-Acetyl-2,5-endomethylenecyclohexene-3 was prepared by the condensation of cyclopentadiene with methylvinylketone. The reaction proceeded even at room temperature. The condensation product had:

B.p. 84-86° at 18 mm, d_4^{20} 1.0090, n_D^{20} 1.4856, M_R 38.72, $C_9H_{12}O$, calculated 38.90.

No distillate was obtained upon distillation with P_2O_5 . Complete resinification occurred.

11. 1-Acetyl-2,5-endoethylenecyclohexene-3 (b.p. 106-107° at 18 mm, n_D^{20} 1.4951) yielded during distillation over P_2O_5 a very small quantity of an oil which distilled in the range 150-200°, d_4^{20} 0.9270, n_D^{20} 1.5096.

A small quantity of high melting acid, the methyl ester of which melted at 129°, was obtained by the oxidation of this distillate.

SUMMARY

1. It was shown that upon distillation with P_2O_5 or with Al_2O_3 at 350-400°, unsaturated hydroaromatic ketones, and in the case of P_2O_5 , aldehydes also, formed during the condensation of diene hydrocarbons and their derivatives with α,β -unsaturated aldehydes and ketones of the fatty series, undergo dehydration with the formation of aromatic compounds.

2. It was suggested that this reaction be used for the determination of the structure of products of the diene synthesis.

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* See Consultants Bureau Translation, page 653.



THERMOCATALYTIC CONVERSIONS OF BUTYLNAPHTHALENES

B. G. Gavrilov and E. N. Nikitina

In recent years a number of works on the thermal and thermocatalytic conversion of alkylbenzenes has been published. At a temperature of 450° and higher, the decomposition of the alkylbenzene molecule into an olefin and benzene occurs [1,2,3,4]:



The works of Dobryansky and his coworkers showed that the simplest alkylbenzenes at temperatures of 150-300° and in the presence of activated natural aluminum silicates transfer unchanged fatty radicals according to the scheme



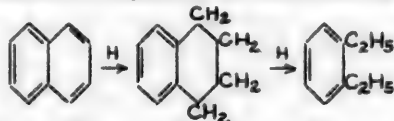
Thus, xylene, ethylbenzene, isopropylbenzene, secondary butylbenzene undergo this conversion to respective extents of 40, 62, 73 and 64% [5,6].

It is of very great interest to study the indicated reaction in representatives of the alkylated condensed aromatic hydrocarbons — the alkyl naphthalenes. In the literature there are only data on the pyrolysis of butylnaphthalene at 650° with the formation of hydrocarbon gases, naphthalene and dinaphthyl [7].

We investigated the thermocatalytic conversion of mono- and di-sec.-butylnaphthalenes over activated natural aluminum silicate catalyst. The experiments with sec.-butylnaphthalene showed that during heating in an auto-clave at 300° for 6 hours the starting material underwent approximately 80% conversion. The chief reaction under these conditions was the conversion of the α -isomer into the thermally more stable β -isomer. A parallel reaction consisted in the formation of dibutylnaphthalene and naphthalene due to the conversion of the butyl radical



There also took place a hydrogenation reaction of naphthalene in statu nascendi, with the formation of tetrahydronaphthalene with subsequent hydrogenation to diethylbenzene with rupture of the polymethylene ring



Butane is formed as the result of another hydrogenation reaction

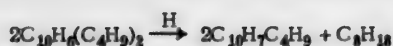


The formation of dinaphthyl can be explained as due to these same causes



The formation of dinaphthyl from naphthalene with the evolution of hydrogen, in view of the greater thermal stability of naphthalene and the comparatively low temperature of our experiments, should be considered as hardly probable.

In the experiment with disecundary butylnaphthalene at a temperature of 280°, the total conversion of the initial hydrocarbon reached approximately 85%. We isolated, in addition to butane, 3,4-dimethylhexane, which arose, evidently, due to the combination of two butyl radicals:



The thus formed mono-secondary-butylnaphthalene in the process of thermocatalytic conversion yielded the same products that were evolved in the first experiment.

As a result of the hydrogenation reactions indicated above, carboids (coke-like substances on the catalyst) were formed, impoverished in hydrogen, and substances contained in the residue during distillation and consisting of a mixture of highly condensed aromatic hydrocarbons. These residues contained 94.93% C and 4.63% H at the same time that the initial monobutylnaphthalene contained 91.16% C and 8.74% H. The possibility of the additional participation in these reactions of the hydrogen, which enters into the composition of the activated aluminum silicates is not excluded.

The results observed by us rather graphically illustrate the process of conversion of petroleum in nature under the influence of heat and the catalytic influence of the clays which accompany the rock. This process proceeds, as is well-known, from the high-molecular-weight and highly cyclized substances, primarily of aromatic structure, via naphthenic hydrocarbons, to methane hydrocarbons as the final conversion products [8].

In our experiments the processes of simplification of the molecules of the initial alkylnaphthalenes are fundamental; in particular, the hydrogenation processes proceed due to the redistribution of hydrogen with the formation of mixed naphthenic-aromatic hydrocarbons (tetrahydronaphthalene), alkylbenzenes (diethylbenzene) and methane hydrocarbons (butane and octane).

In comparing the conversions which were studied of alkylnaphthalenes and alkylbenzenes, the greater reactive capacity of alkylnaphthalenes and lesser strength of the naphthalenic nucleus in comparison with alkylbenzenes should be noted.

EXPERIMENTAL

Activated gumbrin — natural clay of the montmorillonite type — was used as the catalyst. The activation was carried out with 15% hydrochloric acid during heating on a water bath for 12 hours with continuous stirring. After washing off the hydrochloric acid, the catalyst was shaped and dried at 300°.

The mono- and dibutylnaphthalenes were prepared by Tsukervanik's method [9], from naphthalene and *n*-butyl alcohol in the presence of aluminum chloride. The yields of alkylnaphthalenes did not exceed 35%.

α -Sec.-butylnaphthalene. B.p. 272-274°; n_D^{20} 1.5701; d_4^{20} 0.9742.

0.7308 g substance; 8.05 g benzene: Δt 2.55°. 0.3412 g substance: 1.1410 g CO₂; 0.2667 g H₂O. Found %: C 91.16; H 8.74; M 182.3, C₁₄H₁₆. Calculated %: C 91.3; H 8.7; M 184.0

By oxidation during boiling with 5% nitric acid the α -naphthoic acid with a m.p. of 161° was obtained. The picrate melted at 77°.

Di-Sec.-butylnaphthalene. b.p. 310-320°; n_D^{20} 1.5626; d_4^{20} 0.9545.

0.3293 g substance; 8.46 g benzene: Δt 0.839°. 0.2766 g substance: 0.9104 g CO₂; 0.2426 g H₂O. Found %: C 89.76; H 9.81; M 237.9, C₁₈H₂₄. Calculated %: C 90.0; H 10.0; M 240.0.

All the experiments involving the thermocatalytic conversion of butylnaphthalenes were carried out in a steel autoclave, 0.8 liter in capacity, supplied with an electrical heating unit. The temperature was measured with the use of a copper constantan thermocouple, placed in a pocket of the housing of the autoclave. The weight ratio of catalyst and hydrocarbon in all the experiments amounted to 1:1.

After the experiments the catalyst was extracted with petroleum ether. The analysis of the gaseous products was carried out in an All-Union Heat-Engineering Institute apparatus.

Experiment No. 1. 214.8 g of sec.-butylnaphthalene with the same quantity of catalyst was heated for 6 hours at 300°. The pressure was 23 atmospheres, 2.6 liters of gas was obtained.

Analysis of the gas in %: CO₂ 1.0; O₂ 1.2; CO 0.2; H₂ 6.45; C₄H₁₀ 83.95; N₂ (by difference) 7.2. The following basic fractions were isolated by fractional distillation of the liquid products:

Diethylbenzene Fraction. B.p. 177-183°; n_D^{20} 1.4969; d_4^{20} 0.8621.

0.3585 g substance; 16.28 g benzene: Δt 0.880°. 0.1914 g substance; 16.45 g benzene: Δt 0.465°. Found: M 128.4, 128.5, C₁₀H₁₄. Calculated: M 134.

By oxidation of the fraction with an aqueous solution of potassium permanganate phthalic acid was obtained in which the quantity of acid groups was determined.

0.0735 g of acid: 12.41 ml of 0.1 N alkali, 3.70 ml of 0.1 N H_2SO_4 consumed in back titration.
Found %: COOH 53.6, $\text{C}_8\text{H}_4(\text{COOH})_2$. Calculated %: COOH 54.2.

Tetrahydronaphthalene Fraction. B.p. 206-208°; n_D^{20} 1.5410; d_4^{20} 0.9694.

0.1263 g substance; 11.3 g benzene: Δt 0.432°. 0.2136 g substance: 0.7112 g CO_2 ; 0.1728 g H_2O .
Found %: C 90.87; H 9.00; M 130. $\text{C}_{10}\text{H}_{12}$. Calculated %: C 90.91; H 9.09; M 132.

Naphthalene Fraction. B.p. 217-220° The recrystallized substance melted at 80°.

α -Sec.-butylnaphthalene Fraction. B.p. 272-276°; n_D^{20} 1.5706; d_4^{20} 0.9730.

0.2102 g substance; 12.71 g benzene: Δt 0.462°. 0.4374 g substance; 12.74 g benzene: Δt 0.960°.
0.2316 g substance; 0.7728 g CO_2 ; 0.1794 g H_2O . Found %: C 91.05; H 8.67; M 184.0, 182.5. $\text{C}_{14}\text{H}_{16}$.
Calculated %: C 91.3; H 8.7; M 184.

M.p. of α -naphthoic acid 161°.

β -Sec.-butylnaphthalene Fraction. B.p. 285-287°; n_D^{20} 1.5798; d_4^{20} 0.9742.

0.2248 g substance; 19.0 g benzene: Δt 0.327°. 0.4386 g substance; 19.0 g benzene: Δt 0.639°.
0.1816 g substance: 0.6052 g CO_2 ; 0.1454 g H_2O . Found %: C 90.89; H 8.95; M 185.7, 185.3. $\text{C}_{14}\text{H}_{16}$.
Calculated %: C 91.3; H 8.7; M 184.0.

M.p. of β -naphthoic acid 181°.

Dibutylnaphthalene Fraction. B.p. 138-140° (2 mm); n_D^{20} 1.5614; d_4^{20} 0.9540.

1.0846 g substance; 16.85 g benzene: Δt 0.240°. 0.1710 g substance; 15.93 g benzene: Δt 0.235°.
0.1390 g substance: 0.4568 g CO_2 ; 0.1246 g H_2O . Found %: C 89.67; H 10.02; M 234.3, 238.0. $\text{C}_{18}\text{H}_{24}$.
Calculated %: C 90.0; H 10.0; M 240.

Dinaphthyl Fraction. B.p. 227-229° (2 mm). M.p. 186.5°.

0.0652 g substance: 13.56 g benzene: Δt 0.098°. 0.0794 g substance; 13.56 g benzene: Δt 0.120°.
Found: M 251.7, 250.3. $\text{C}_{20}\text{H}_{14}$. Calculated: M 254.

The values for the yields obtained by fractional distillation of the substances are set forth in Table 1.

Experiment No. 2. 184 g of di-sec.-butylnaphthalene was heated for 16 hours at 275°. The maximum pressure was 31 atm. 3.5 liters of gas was obtained. The analysis of the gas in %: CO_2 0.5; O_2 2.05; CO 1.15; H_2 12.6; C_4H_{10} 70.1; N_2 12.6.

The following fractions were obtained by fractional distillation of the liquid products.

Octane Fraction. B.p. 117-119°; n_D^{20} 1.4048; d_4^{20} 0.7199.

0.1962, 0.3477 g substance; 15.52, 15.52 g benzene: Δt 0.595, 1.050°. Found: M 108.9, 109.4. C_8H_{18} .
Calculated: M 114.

Diethylbenzene Fraction. B.p. 177-183°; n_D^{20} 1.4966; d_4^{20} 0.8622.

0.2042, 0.1964 g substance; 13.68, 12.76 g benzene: Δt 0.583, 0.594°. Found: M 131.2, 132.8. $\text{C}_{10}\text{H}_{14}$.
Calculated: M 134.

Tetrahydronaphthalene Fraction. B.p. 206-208°; n_D^{20} 1.5412; d_4^{20} 0.9690.

0.2462, 0.1978 g substance; 14.33, 13.47 g benzene: Δt 0.685, 0.574°. Found: M 128.7, 131.1. $\text{C}_{10}\text{H}_{12}$.
Calculated: M 132.

Naphthalene Fraction. B.p. 217-220° The recrystallized substance melted at 80.2°.

α -Sec.-butylnaphthalene Fraction. B.p. 272-276°; n_D^{20} 1.5710; d_4^{20} 0.9730.

0.2688, 0.4692 g substance; 12.99, 12.99 g benzene: Δt 0.605, 1.008°. Found: M 183.7, 184. $\text{C}_{14}\text{H}_{16}$.
Calculated: M 184.

β -Sec.-butylnaphthalene Fraction. B.p. 285-287°; n_D^{20} 1.5792; d_4^{20} 0.9748.

0.1674, 0.1578 g substance; 13.14, 12.62 g benzene: Δt 0.348, 0.340°. Found: M 187.8, 188.7. $\text{C}_{14}\text{H}_{16}$.
Calculated: M 184.

TABLE 1

Substance	Yield	
	In g	In % of the butylnaphthalene taken
Diethylbenzene	5.8	2.7
Tetrahydronaphthalene	4.9	2.2
Naphthalene	47.1	22.1
α -Sec.-butylnaphthalene	42.2	19.7
β -Sec.-butylnaphthalene	37.7	17.2
Dibutylnaphthalene	9.2	4.3
Dinaphthyl	8.5	3.9
Coke on the catalyst	14.2	6.6
Residue	27.4	12.9
Loss	15.5	7.3
Total:	212.5	98.9

TABLE 2

Fraction	Yield	
	In g	In % of the dibutylnaphthalene taken
Octane	17.5	9.5
Diethylbenzene	7.1	4.4
Tetrahydronaphthalene	11.2	6.1
Naphthalene	26.1	14.2
α -Sec.-butylnaphthalene	19.6	10.7
β -Sec.-butylnaphthalene	15.0	8.2
Dibutylnaphthalene	28.5	15.5
Dinaphthyl	7.9	4.3
Coke on the catalyst	21.5	11.7
Residue after fractional distillation	13.8	7.2
Loss	13.0	6.8
Total:	181.4	98.6

Dibutylnaphthalene Fraction. B.p. 138-140° (2 mm); n_D^{20} 1.5610; d_4^{20} 0.9544.

0.2064, 0.5140 g substance; 12.06, 12.06 g benzene; Δt 0.370, 0.900°. Found: M 237.3, 243.0. $C_{18}H_{24}$. Calculated: M 240.

Dinaphthyl Fraction. B.p. 227-229° (2 mm). M.p. 186.2°.

0.1912, 0.2142 g substance; 14.10, 13.75 g benzene; Δt 0.278, 0.322°. Found: M 250, 247.6. $C_{20}H_{14}$. Calculated: M 254.

The values of the yields obtained by fractional distillation of the substances are set forth in Table 2.

SUMMARY

1. The thermocatalytic conversions of mono- and di-sec.-butylnaphthalenes over natural aluminum silicate catalyst were studied.

In addition to the typical alkylbenzene reactions involving the migration of unchanged fatty radicals, a number of other reactions were observed. The most characteristic of them were the formation of diethylbenzene, tetrahydronaphthalene, dinaphthyl and butane, proceeding via the redistribution of hydrogen and also the formation of octane (3,4-dimethylhexane), evidently due to the combination of butyl radicals.

The results obtained confirm the general rule which specifies the following direction for the conversion processes of petroleum in nature: aromatic hydrocarbons \rightarrow naphthenic hydrocarbons \rightarrow methane hydrocarbons.

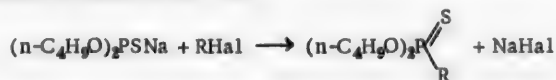
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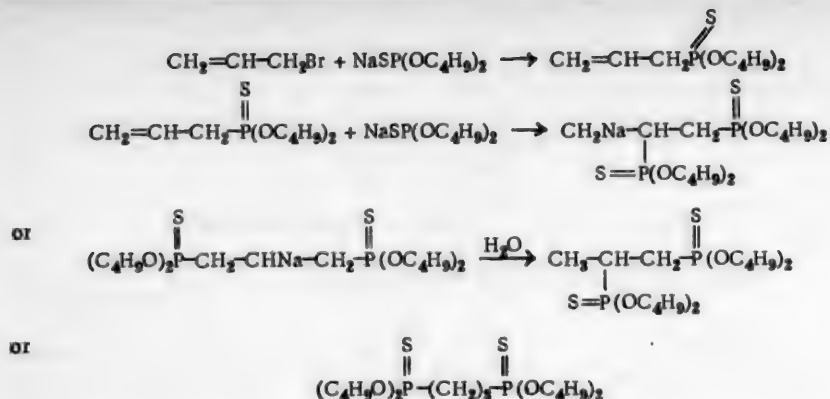
ACTION OF ALKYL HALIDES AND ALLYL BROMIDE ON SODIUM DIBUTYLTHIOPHOSPHITE

A. N. Pudovik and K. A. Kovyryzina

The action of alkyl halides on salts of dialkylphosphorous acids has been studied in sufficient detail at the present time, and is one of the most important methods of synthesizing the esters of alkylphosphinic acids. The reactions between the salts of dialkylphosphorous acids and allyl halide compounds was studied by one of us only in the last few years, and led to very interesting and important conclusions. It was shown that, depending on the presence or absence in the reaction mixture of excess dialkylphosphorous acid or of solvent, the reaction leads to different results [1]. In the first case, allylphosphinic esters are formed in quantitative yield; in the second case, in addition to the allylphosphinic esters, the products of addition to them of dialkylphosphorous acid molecules were isolated primarily, and in certain cases exclusively. The possibility of direct addition of dialkylphosphorous acids at the double bond of allylphosphinic esters was confirmed in special experiments. The results obtained were the basis for working out a new method of synthesizing the esters of phosphinic and thiophosphinic acids, consisting in the addition of various reagents to unsaturated compounds of the electrophile type [2]. In the development and extension of works previously carried out, we studied the reaction between dialkylthiophosphites, alkyl halides and allyl halide compounds. This investigation, as it appeared to us, could be of interest both from the point of view of the study of the mechanism of the indicated reactions, and for working out a method of synthesizing esters of alkylthiophosphinic acids. The esters of alkylthiophosphinic acids have hardly been studied at all until very recently. It was only in 1952 that Arbuzov and Rizpolozhensky [3] and Razumov and Mukhacheva and Sim-Do-Khen [4] proposed an accessible method for preparing them, consisting of the addition of sulfur to esters of alkylphosphinous acids. In a second variant of this method, the preparation of esters of alkylthiophosphinic acids was proposed via the addition of sulfur to alkylchlorophosphine with subsequent treatment of the product formed with sodium alcoholate. As a result of the working out of a method of synthesis of dialkylthiophosphorous acids, the possibility of synthesizing esters of alkylthiophosphinic acids with the aid of alkaline metal salts of dialkylthiophosphorous acids became evident. Kabachnik and Mastyukova carried out a reaction between diethylsodium diethylthiophosphite, ethyl iodide, benzyl chloride and chloroacetic ester [5]. We also, before entering upon the study of the reactions between dialkylthiophosphites and halogen allyl compounds, carried out a number of reactions with alkyl halides. In contrast to the diethylthiophosphites, the alkaline metal salts of diethylthiophosphorous acid were poorly soluble in ether and benzene. The experiments carried out by us with ethyl iodide and the sodium and lithium salts of diethylthiophosphorous acid led to the formation of the ethyl ester of ethylthiophosphinic acid. However, the yields of it were insufficiently high; therefore in further experiments we substituted sodium diethylthiophosphite for sodium dibutylthiophosphite. The latter was considerably more soluble in ether and benzene, and the reaction with them proceeded almost as readily as with sodium diethylphosphite. The precipitate of sodium bromide formed in the reaction process was filtered off or eliminated by treatment of the reaction mixture with water. Experiments were carried out with ethyl iodide, propyl iodide, butyl bromide, and chloromethylbutyl ether. In all cases the butyl esters of the corresponding alkylthiophosphinic acids were isolated in yields of 60-70%.



As a result of the reaction between sodium dibutylthiophosphite and allyl bromide two products were obtained: a low boiling product (b.p. 120° at 3 mm) which appeared to be the butyl ester of allylthiophosphinic acid, and a high boiling product (b.p. 207° at 3 mm), corresponding, according to the analytical data for sulfur and phosphorus, to di(dibutylthiophosphono)propane. The course of the reaction can be represented by the following scheme:



The structure of di(dibutylthiophosphono)propane, as regards the choice of one of the two possible isomeric forms, remains as yet unestablished. Thus, the reaction of sodium dibutylthiophosphite with allyl bromide, by analogy with the reactions of dialkylphosphites, also proceeds in two phases: initially a substitution reaction proceeds, and then, depending on the ratio of reagents and the conditions under which the experiment is carried out, the addition reaction of dibutylthiophosphorous acid at the double bond of allylthiophosphinic ester proceeds.

EXPERIMENTAL

Action of Ethyl Iodide on Sodium Diethylthiophosphite

13 g of diethylthiophosphorous acid was slowly introduced in drops into 2 g of metallic sodium, pressed in the form of wires, in 200 ml of dry toluene. The reaction was initially carried out in the cold, and then during heating on a water bath and with continuous stirring until the evolution of hydrogen ceased. The sodium derivative was evolved in the reaction process in the form of a voluminous, finely crystalline, white precipitate. 20 g of ethyl iodide was slowly added to the thus-obtained sodium derivative during uninterrupted stirring. The reaction mixture was heated on a water bath for 3 hours. The sodium iodide was filtered off, the toluene distilled off at 90 mm; the residue, which consisted of a thick, oily liquid of an unpleasant odor, was vacuum distilled from an Arbuzov flask. As a result of two distillations, 6.8 g of diethyl ester of ethylthiophosphinic acid with a b.p. of 79-80° at 12 mm; n_D^{20} 1.4555; d_4^{20} 1.0338, was obtained.

0.1542, 0.1506 g substance: 40.9, 40.5 ml NaOH ($T = 0.0226$). 0.1569, 0.1642 g substance: 0.2027, 0.2109 g BaSO₄. Found %: P 16.60, 16.83; S 17.82, 17.61. C₆H₁₂O₂PS. Calculated %: P 17.03; S 17.57.

The product obtained by us was identical according to its properties with that obtained by Kabachnik and Mastyukova [5].

Action of Ethyl Iodide on Sodium Dibutylthiophosphite

Sodium dibutylthiophosphite was prepared from 14 g of dibutylthiophosphorous acid, 2 g of sodium and 250 ml of absolute ether. The unreacted sodium was removed mechanically from the solution with the aid of long glass needles. 14.8 g of ethyl iodide was then slowly introduced in drops into the sodium dibutylthiophosphite solution during stirring with a mechanical stirrer. The reaction mixture was heated on a water bath for 3 hours. After cooling in a flask, a small (but sufficient for dissolving the sodium iodide precipitate which had formed) quantity of water was added, after which the entire reaction mixture was transferred to a separatory funnel. The ethereal layer was separated off and dried with calcium chloride. After distilling off the ether, the residue was vacuum distilled. 9.6 g of the dibutyl ester of ethylthiophosphinic acid with a b.p. of 97-98° at 2 mm; n_D^{20} 1.4510; d_4^{20} 0.9768, was obtained.

0.1156, 0.1252 g substance: 23.4, 25.6 ml NaOH ($T = 0.0226$). 0.1666 g substance: 0.1497 g BaSO₄. Found %: P 12.68, 13.09; S 13.13. C₁₀H₂₀O₂PS. Calculated %: P 13.03; S 13.44.

Action of Propyl Iodide on Sodium Dibutylthiophosphite

10 g of propyl iodide was slowly introduced in drops into a stirred ethereal solution of sodium dibutylthiophosphite, prepared from 9.8 g of dibutylthiophosphorous acid, 1.3 g of sodium and 250 ml of absolute ether. After the reaction mixture had been heated for three hours on a water bath, it was cooled and treated with water. After separation and drying of the ethereal layer, the ether was distilled off, and the residue vacuum distilled. 5.9 g of the dibutyl ester of propylthiophosphinic acid with a b.p. of 103-104° at 2 mm; n_D^{20} 1.4580; d_4^{20} 0.9772, was obtained.

0.1340 g substance: 70.7 ml NaOH ($T = 0.00880$). 0.1304, 0.1544 g substance: 0.1217, 0.1464 g BaSO_4 . Found %: P 12.86; S 12.82, 13.01. $\text{C}_{11}\text{H}_{25}\text{O}_2\text{PS}$. Calculated %: P 12.56; S 12.70.

Action of Butyl Bromide on Sodium Dibutylthiophosphite

11 g of butyl bromide was introduced in drops into an ethereal solution of sodium dibutylthiophosphite, prepared from 10 g of dibutylthiophosphorous acid, 1.3 g of sodium and 250 ml of ether. The subsequent reaction and treatment of the reaction mixture were carried out analogously to those described in the preceding experiments. As a result 6.7 g of the dibutyl ester of butylthiophosphinic acid with a b.p. of 108-109° at 2 mm; n_D^{20} 1.4654; d_4^{20} 0.9780 was obtained.

0.1410 g substance: 25.1 ml NaOH ($T = 0.0226$). 0.1115, 0.1205 g substance: 0.1012, 0.1032 g BaSO_4 . Found %: P 11.14; S 12.46, 12.32. $\text{C}_{12}\text{H}_{27}\text{O}_2\text{PS}$. Calculated %: P 11.65; S 12.03.

Action of Chloromethylbutyl Ether on Sodium Dibutylthiophosphite

The ethereal solution of sodium dibutylthiophosphite was prepared from 9.9 g of dibutylthiophosphorous acid, 1.5 g of sodium and 250 ml of ether. The excess sodium was eliminated from the solution mechanically with the aid of a glass needle. The reaction was carried out with 10 g of chloromethylbutyl ether. After completion of the reaction, the reaction mixture was treated with water, the ethereal solution was dried with sodium sulfate, the ether was distilled off on a water bath, the residue vacuum distilled. 8.6 g of the dibutyl ester of butoxymethylthiophosphinic acid with a b.p. of 146-148° at 5 mm; n_D^{20} 1.4482; d_4^{20} 0.9806, was obtained.

0.1340, 0.1412 g substance: 21.63, 22.66 ml NaOH ($T = 0.0226$). 0.1456, 0.1170 g substance: 0.1185, 0.0963 g BaSO_4 . Found %: P 10.10, 10.04; S 11.18, 10.30. $\text{C}_{22}\text{H}_{45}\text{O}_3\text{PS}$. Calculated %: P 10.47, S 10.81.

Action of Sodium Dibutylthiophosphite on Allyl Bromide

18.5 g of allyl bromide was introduced in drops into a stirred ethereal solution of sodium dibutylthiophosphite, prepared from 20 g of dibutylthiophosphorous acid, 2 g of sodium and 300 ml of absolute ether. The reaction mixture was heated on a water bath for 2 hours, treated with water, the ethereal layer was dried with sodium sulfate, the ether driven off, and the residue vacuum distilled. The following were obtained: a) 10.1 g of the dibutyl ester of allylthiophosphinic acid with a b.p. of 120° at 3 mm; n_D^{20} 1.4710; d_4^{20} 0.9858.

0.1248, 0.1418 g substance: 23.94, 26.95 ml NaOH ($T = 0.0226$). 0.1402, 0.1436 g substance: 0.1348, 0.1352 g BaSO_4 . Found %: P 12.00, 11.89; S 13.20, 12.96. $\text{C}_{11}\text{H}_{25}\text{O}_2\text{PS}$. Calculated %: P 12.40; S 12.80.

b) 2.6 g of di(dibutylthiophosphono)propane in the form of colorless, viscous liquid with a b.p. of 207° at 3 mm; n_D^{20} 1.4643.

0.1312, 0.1278 g substance: 27.81, 27.80 ml NaOH ($T = 0.0226$). 0.1314, 0.1196 g substance: 0.1361, 0.1261 g BaSO_4 . Found %: P 13.26, 13.61; S 14.22, 14.48. $\text{C}_{19}\text{H}_{41}\text{O}_4\text{P}_2\text{S}_2$. Calculated %: P 13.33; S 13.92.

SUMMARY

1. The action of alkyl halides on sodium dibutylthiophosphite was studied. The dibutyl esters of the following were synthesized: ethyl-, n-propyl-, n-butyl-, and butoxymethylthiophosphinic acids.

2. It was shown that during the action of sodium dibutylthiophosphite on allyl bromide, along with the substitution reaction, an addition reaction of dibutylthiophosphorous acid at the double bond of the allylthiophosphinic ester also proceeds.

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* See Consultants Bureau Translation, page 2107.

** See Consultants Bureau Translation, 423.

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REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

VII. ESTERS OF α -HYDROXY(6-QUINOLYL)METHYLPHOSPHINIC ACID

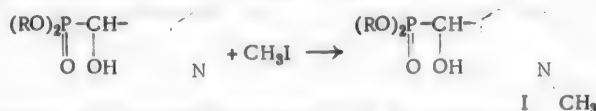
V. S. Abramov and A. S. Kapustina

The reaction of dialkylphosphorous acids with carbonyl compounds [1] was successfully extended by us to aldehydes of the heterocyclic series. 6-Quinoline aldehyde reacts with various dialkylphosphorous acids and forms the corresponding esters of α -hydroxy(6-quinolyl)-methylphosphinic acid, according to the scheme



We carried out the reaction of 6-quinoline aldehyde with dimethyl-, diethyl-, dipropyl-, diisopropyl-, dibutyl-, disobutyl-, and diallylphosphorous acids; consequently, R in the scheme will respectively, be CH_3 , C_2H_5 , C_3H_7 , C_3H_7 -iso, C_4H_9 , C_4H_9 -iso, and C_5H_5 . The reaction proceeds rapidly with the evolution of heat. Colorless viscous syrups are formed. 6-Quinoline aldehyde was selected by us as the carbonyl compound because we expected to obtain the esters of α -hydroxy(6-quinolyl)methylphosphinic acid in the crystalline form. This was important for readily obtaining them in the pure form, since the application of fractional distillation for the purification of such comparatively high molecular weight compounds could not give positive results. We had previously shown that the esters of α -hydroxyalkylphosphinic acids are decomposed during distillation (heating) into the initial substances, and the more readily for a given dialkylphosphorous acid, the higher the total molecular weight of the ester, and the higher the weight of the radical bound to the phosphorus atom [2].

Our expectations of obtaining crystalline products were not correct. Only one isopropyl ester of α -hydroxy(6-quinolyl)methylphosphinic acid with a m.p. of 119-120° was obtained in the crystalline form. We had, moreover, planned in the case of formation of noncrystalline syrups, their conversion into ammonium derivatives or the preparation of their picrates. The latter we proposed to isolate in the crystalline state. The few experiments carried out by us involving the action of alkyl halides on the esters of α -hydroxy(6-quinolyl)methylphosphinic acids with the object of preparing halogen substituted ammonia



were not crowned with success — crystalline derivatives were not obtained.

By the reaction of the esters of α -hydroxy(6-quinolyl)methylphosphinic acid with picric acid, excellently crystallizing picrates were formed. The picrates were obtained either directly or by pouring the esters of α -hydroxy(6-quinolyl)methylphosphinic acid with a saturated solution of picric acid in alcohol or after boiling the solution for a brief time. The picrates consisted of well-formed, needle-like crystals with an orange color. The picrates were recrystallized from ethyl alcohol; methyl and butyl alcohols were also employed.

The results of the reactions investigated, involving the reaction of 6-quinoline aldehyde with various dialkylphosphorous acids, and also the characteristics of the picrates obtained, and of the esters of α -hydroxy(6-quinolyl)methylphosphinic acid formed, are set forth in the table.

EXPERIMENTAL

Reaction of Dialkylphosphorous Acids with 6-Quinoline Aldehyde

An equimolecular mixture of the dialkylphosphorous acid and 6-quinoline aldehyde was prepared, which was then carefully heated to complete solution of the 6-quinoline aldehyde in the acid. The solution was cooled to room temperature or to a temperature at which crystallization began. The temperature of the solution

Dialkylphosphorous acid	Quantity of reacting substances (in g)		Increase in temperature (in °)	Esters obtained	Yield of ester (in %)	M.p. of the picrate (in °)	Yield of picrate (in g)	Content of phosphorus in the picrate (in %)	
	Acid	6-Quinoline aldehyde						Calculated	Found
$(\text{CH}_3\text{O})_2\text{POH}$	2.2	3.0	40-67		75.0	170-171	7.3	6.02	5.58, 5.86
$(\text{C}_2\text{H}_5\text{O})_2\text{POH}$	1.8	2.0	19-96		44.5	152	3.0	5.87	5.51, 5.32
$(\text{C}_3\text{H}_7\text{O})_2\text{POH}$	3.4	3.2	42-105		53.2	151-152	6.0	5.57	5.43, 5.52
iso- $(\text{C}_3\text{H}_7\text{O})_2\text{POH}$	1.7	1.6	36-62		39.0	146-147	2.2	5.57	5.68, 5.65
$(\text{C}_4\text{H}_9\text{O})_2\text{POH}$	3.9	3.14	45-65		62.7	157-158	7.3	5.30	5.21, 5.35
iso- $(\text{C}_4\text{H}_9\text{O})_2\text{POH}$	3.9	3.14	23-67		51.5	150-150.5	6.0	5.30	5.24, 5.35
$(\text{C}_8\text{H}_5\text{O})_2\text{POH}$	3.9	3.14	35-83		84.5	167	9.2	5.61	5.40

• The crystalline substance has a m.p. of 119-120°. Found %: P 9.44, 9.25. $\text{C}_{18}\text{H}_{15}\text{O}_2\text{NP}$. Calculated %: P 9.65.

was measured and a freshly prepared saturated solution of sodium methylate was added in drops. After the addition, an increase in temperature was observed. The product which formed ordinarily consisted of a transparent, viscous syrup. The product was cooled to a low temperature (with a mixture of snow and salt), but only the isopropyl ester of α -hydroxy(6-quinolyl)methylphosphinic acid was obtained in the crystalline state. After recrystallization from cyclohexane, its melting point was 119-120°.

The noncrystallized syrups were mixed with an equimolecular quantity of picric acid dissolved in alcohol. A precipitate of the picrate ordinarily settled out at once. Only in isolated cases was an insignificant amount of heating carried out. The picrate was recrystallized from methyl, ethyl or butyl alcohol. The melting points of the picrates are set forth in the table. The phosphorus content of the picrates was determined. The analysis and yields of the esters are also set forth in the table.

SUMMARY

The action of dialkylphosphorous acids on 6-quinoline aldehyde was studied. Seven new esters of α -hydroxy-(6-quinolyl)methylphosphinic acid were obtained and isolated from the reaction products in the form of the picrates. The isopropyl ester of α -hydroxy(6-quinolyl)methylphosphinic acid was prepared in the form of colorless, regular crystals with a m.p. of 119-120°.

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• See Consultants Bureau Translation, page 709.

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10-2-2000

INVESTIGATIONS IN THE FIELD OF QUINOLINE DERIVATIVES

XI. SYNTHESIS OF LEPIDINE AND ITS DERIVATIVES FROM ACETYLATED ARYLAMINES

B. I. Ardashev and B. A. Tertov

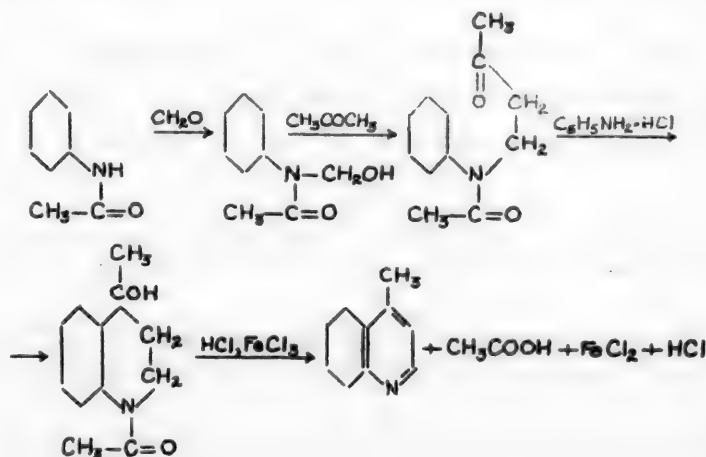
We previously noted that α -substituted quinolines are considerably more accessible than γ -substituted quinolines [1]. The Knorr method is ordinarily employed for the synthesis of lepidine and its derivatives and gives excellent yields. The conversion from hydroxyderivative to lepidine was successfully solved in 1936 by G. I. Mikhailov by the action of phosphorus oxychloride, with subsequent reduction of the chloro derivative by tin and hydrochloric acid [2, 3].

However, even though there have been substantial refinements in the Knorr reaction, it retains its basic defect — the fact that it proceeds in several stages and is rather unwieldy and prolonged. Other methods are also practically difficult on account of the insufficient accessibility of the starting materials, or unsuitable as a consequence of the low yields of lepidine, the long time required for accomplishing the reaction, and for a number of other reasons [3].

Beyer's method, by which lepidine and its derivatives can be obtained from primary aromatic amines, formaldehyde and acetone [4], i.e., from readily accessible starting materials, gives low yields of lepidine and its substituted derivatives, which do not exceed 4-5% of the theoretical [5]. As a result, a sufficiently convenient preparative method for the synthesis of lepidine and its derivatives has not been achieved up to the present time. One of the important causes of the low yields of lepidine bases in the Beyer reaction is the great activity of formaldehyde, which gives a number of side products, including an aminomethylated aromatic nucleus. In the course of synthesizing lepidine and its derivatives by this method, we satisfied ourselves that addition of amine salt increases the yield of quinolinic base by at least 50%. It should be noted that the amino ketones, which appear to be intermediate products in the Beyer reaction [7], form unstable compounds with arylamines [8] which, are cyclized when they decompose. This mechanism for the Beyer reaction leads to the conclusion that while it is being carried out, it is expedient to have an excess of the reacting amine in the reaction mixture for possibly a more prolonged time. It was shown to be beneficial to introduce acetylated amines into the reaction as starting materials, since, as is well known, this diminishes the mobility of the hydrogens of the aromatic nucleus and makes more difficult the formation of substitution products, and thereby facilitates the cyclization reaction.

As a result of the experiments carried out, higher yields were achieved than by the Beyer method [4]. It was established that our method can be employed to obtain various lepidine derivatives; for example, by introducing methylethyl ketone into the reaction, the comparatively slightly accessible 3,4-dimethylquinolines are formed. Amines which are disubstituted in the aromatic nucleus give higher yields of quinolines.

The reaction mechanism, with reference to lepidine, is basically as follows [9]:



EXPERIMENTAL

Initially the experiments were set up to obtain lepidine and 6-methyllépidine from anhydroformaniline and anhydroformtoluidine. These experiments showed that addition of ferric chloride to the reaction increased the lepidine yield. It was then established that upon the addition of the hydrochlorides of the corresponding amine, the yield was increased at least 50%. Thus, lepidine is formed from anhydroformaniline in a yield of 6-8% of the theoretical, while by the addition of aniline hydrochloride (better in a total quantity of 2 moles of amine per 1 mole of anhydro-base) the yield was increased to 12%. 4,6-Dimethylquinoline can be obtained from p-toluidine in this way in a yield of 18% of the theoretical. The base was purified by decomposing the sulfate. The following method of preparing lepidine and its derivatives was subsequently worked out.

Synthesis of Lepidine

20 g of acetanilide, 20 ml of acetone, 30 ml of alcohol, 25 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5 ml of concentrated hydrochloric acid were placed in a round-bottomed flask. The flask was supplied with a reflux condenser and a dropping funnel with an alcoholic solution of paraformaldehyde.* The mixture was heated to boiling and the solution was added from the dropping funnel over a period of 40 minutes. After this, the mixture was boiled for 20-25 minutes more, 5 ml of concentrated hydrochloric acid was added to the reaction flask, and the contents of the flask were boiled for an additional 30 minutes. After distilling off the alcohol, acetone, acetic acid and ethyl acetate at a temperature up to 100-105° (the bulb of the thermometer was submerged in the boiling reaction mixture) and rendering the mixture alkaline with concentrated sodium hydroxide solution, the base was steam distilled off.

The lepidine was purified from the aniline by means of diazotization or boiling a mixture of the ether-extracted base with 5 ml of acetic anhydride, with subsequent steam distillation. The yield of lepidine, with b.p. 258-263°, was 3.9 g (18.4%). Lepidine picrate melted at 212°. A mixed sample with known lepidine picrate did not display melting point depression.

Synthesis of 4,6-Dimethylquinoline

4,6-Dimethylquinoline, prepared from 20 g of p-acetyl-toluidine, analogously to the preceding, was isolated in a quantity of 5.2 g (24.8%), with b.p. 263-270°. The picrate melted at 237°.

Synthesis of 4,6,8-Trimethylquinoline

20 g of aceto-m-xylidide, 20 ml of acetone, 30 ml of alcohol, 25 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 8 ml of concentrated hydrochloric acid (d 1.19) were placed in a round-bottomed flask. The mixture was heated to boiling and through a dropping funnel, inserted in a reflux condenser, a solution of 5 g of paraform in 30 ml of alcohol was continuously added dropwise over a period of 50 minutes. The mixture was boiled for 20 minutes more, after which 5 ml of concentrated hydrochloric acid was added to the flask and the boiling was continued for an hour. After cooling, the mixture was rendered alkaline with 40% sodium hydroxide solution, 30 ml of alcohol was added, and the iron hydroxide which settled out was filtered off. The filtrate was diluted with water to a volume of 400 ml, and the base which was evolved was extracted with ether. The ether was distilled off, the 215-310° fraction was collected, boiled with 100 ml of 15% hydrochloric acid to saponify unreacted aceto-m-xylidide. A saturated solution of potassium ferrocyanide was added to the hydrochloric acid solution of the bases until no more precipitate settled out. The precipitate was filtered off and decomposed with alkali, and the oil which was evolved was extracted with ether. After distilling off the ether, the base was fractionally distilled in the 270-280° range in a quantity of 7 g (33%); m.p. 51°. After recrystallization from a small quantity of petroleum ether, the m.p. was 57°. The picrate, precipitated from alcohol, had m.p. 209°.

0.1030 g sub.: 13 ml N_2 (21°, 754 mm). Found %: N 14.19. $\text{C}_{12}\text{H}_{13}\text{N} \cdot \text{C}_6\text{H}_5(\text{NO}_2)_3\text{OH}$. Calculated %: N 14.00.

The dichromate salt of the base was precipitated in the form of fine yellow needles.

0.1495 g sub.: 0.0412 g Cr_2O_3 . Found %: Cr_2O_3 27.55. Calculated %: Cr_2O_3 27.14.

SUMMARY

1. Lepidine, 6-methyllépidine and 6,8-dimethyllépidine, which was hitherto undescribed in the literature, were prepared by acetylation of aromatic amines, formaldehyde and acetone in alcoholic solution in the presence of ferric

* 6 g of paraformaldehyde was placed in an ampoule, 35 ml of ethyl alcohol and 2-3 drops of hydrochloric acid (d 1.19) were added, the ampoule was sealed, and the contents heated on a water bath until the paraform dissolved.

chloride in yields, respectively of 18%, 25% and 33%.

2. A method which was worked out for the synthesis of lepidine and its derivatives and which requires comparatively little time (4-5 hours) can be recommended as a preparative method for obtaining them.

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CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXIV. CATALYTIC SYNTHESIS OF 2-(p-METHYLPHENYL)-QUINOLINE AND ITS DERIVATIVES

N. S. Kozlov and N. I. Panova

A new method of synthesizing α -phenyl derivatives of quinoline via the joint condensation of an aromatic amine and an aromatic aldehyde with acetylene in the presence of copper or mercury salts [1] was described earlier in the work of one of us. A mechanism for this reaction was also then proposed and has been confirmed by our present work. The method proposed is a new method of synthesizing various derivatives of α -phenylquinoline themselves if various aromatic amines and aldehydes are introduced in the reaction.

Up to the present time, the following aromatic aldehydes have been introduced in the reaction of joint condensation of an aromatic amine and an aromatic aldehyde with acetylene: benzaldehyde, anisaldehyde and piperonal [2]. In the present work, the catalytic condensation of acetylene with various aromatic amines and p-toluyaldehyde was studied. The following aromatic amines were studied: aniline, p-toluidine, p-anisidine and p-phenetidine. As a result of the work which we have carried out, 2-(p-methylphenyl)-quinoline and a number of its derivatives have been synthesized; these compounds had not been described in the literature and were prepared by us for the first time.

EXPERIMENTAL

Synthesis of 2-(p-Methylphenyl)-quinoline

Acetylene was passed into a reaction mixture consisting of 23 g of aniline, 18 g of p-toluyaldehyde, 50 ml of alcohol and 5 g of mercuric chloride until the mixture was saturated. 2 g more of mercuric chloride was then introduced, and the saturation continued until cessation of acetylene absorption. About 20 hours were required for this. A 10% sodium hydroxide solution was then introduced into the reaction mass until it had an alkaline reaction and the alcohol and aromatic amine which had not entered into the reaction were steam distilled off. The reaction product consisted of a solid, resinous substance with a brown color. The following fractions were obtained by vacuum distilling it at 2.5 mm: 1st 80-150°, 3 g; 2nd 150-190°, 8 g; residue 10 g.

The second fraction crystallized on cooling; 5 g of a crystalline substance was obtained which had a m.p. of 81-82° after recrystallization from alcohol.

The yield of 2-(p-methylphenyl)-quinoline amounted to 15.2% of the aldehyde taken.

0.0854, 0.0957 g sub.: 4.04, 4.43 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.62, 6.48. $\text{C}_{16}\text{H}_{13}\text{N}$. Calculated %: N 6.39.

The substance obtained formed a picrate with a m.p. of 197-198° (with decomposition), and a platinate.

0.1038 g sub.: 0.240 g Pt. Found %: Pt 23.12. $(\text{C}_{16}\text{H}_{13}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$. Calculated %: Pt 23.01.

Synthesis of 6-Methyl-2-(p-methylphenyl)-quinoline

28.0 g of p-toluidine was taken. The rest of the reagents were taken in the same quantities as indicated above. The isolation of the reaction products was carried out in the same way as in the preceding experiment. The reaction product consisted of a resinous substance. The following fractions were obtained by its vacuum distillation at 2.5 mm: 1st 90-150°, 2 g; 2nd 150-200°, 9 g; residue 9 g.

The second fraction crystallized on cooling. 6.0 g of a crystalline substance was obtained which had a m.p. of 137-138° after recrystallization from alcohol.

0.0968, 0.1263 g sub.: 4.23, 5.41 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.12, 5.99. $\text{C}_{17}\text{H}_{15}\text{N}$. Calculated %: N 6.00.

The substance obtained formed a picrate with a m.p. of 200-201°, and a platinate.

0.0950 g sub.: 0.213 g Pt. Found %: Pt 22.42. $(\text{C}_{17}\text{H}_{15}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$. Calculated %: Pt 22.27.

The yield of 6-methyl-2-(p-methylphenyl)-quinoline amounted to 17.1% of the aldehyde taken.

Synthesis of 6-Methoxy-2-(p-methylphenyl)-quinoline

It was prepared from 30 g of p-anisidine by the method described above. The reaction product consisted of a resinous substance. Distillation at 2.5 mm yielded the following fractions: 1st 80-180°, 3 g; 2nd 180-230°, 10 g; residue 10 g.

7.7 g of a crystalline substance was obtained from the second fraction on cooling, which after recrystallization from alcohol had a m.p. of 150-151°.

0.1150, 0.1130 g sub.: 4.53, 4.56 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 5.51, 5.65. $\text{C}_{17}\text{H}_{15}\text{ON}$. Calculated %: N 5.62.

The substance obtained formed a picrate with a m.p. of 207-208°, and a platinate.

0.1020 g sub.: 0.016 g Pt. Found %: Pt 21.17. $(\text{C}_{17}\text{H}_{15}\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6$. Calculated %: Pt 21.48.

The yield of 6-methoxy-2-(p-methylphenyl)-quinoline was 20.6% of the aldehyde taken.

Synthesis of 6-Ethoxy-2-(p-methylphenyl)-quinoline

25 g of p-phenetidine was condensed with 15 g of p-toluyaldehyde and acetylene under the conditions described above. By distillation of the resinous substance obtained in a vacuum at 2.5 mm the following fractions were obtained: 1st 90-140°, 3 g; 2nd 150-210°, 10 g; residue 9 g.

5 g of a crystalline substance was obtained by cooling the second fraction and had a m.p. of 138-139° after recrystallization from alcohol.

0.1792, 0.1046 g sub.: 6.74, 3.77 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 5.26, 5.04. $\text{C}_{18}\text{H}_{17}\text{ON}$. Calculated %: N 5.31.

The picrate with a m.p. of 191-192°, and a platinate, were formed.

0.1120 g sub.: 0.0231 g Pt. Found %: Pt 20.62. $(\text{C}_{18}\text{H}_{17}\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6$. Calculated %: Pt 20.84.

The yield of 6-ethoxy-2-(p-methylphenyl)-quinoline amounted to 15.2% of the aldehyde taken.

We, incidentally, prepared from p-toluyaldehyde and a number of aromatic amines the Schiff bases, the m.p. of which were: 1) from p-toluidine 91-92°, 2) from p-phenetidine 105-107°; 3) from p-anisidine 86-87°.

SUMMARY

By joint catalytic condensation of acetylene and p-toluyaldehyde with aniline, p-toluidine, p-anisidine and p-phenetidine, the following compounds: 2-(p-methylphenyl)-quinoline, 6-methyl-2-(p-methylphenyl)-quinoline, 6-methoxy-2-(p-methylphenyl)-quinoline and 6-ethoxy-2-(p-methylphenyl)-quinoline were prepared for the first time and described.

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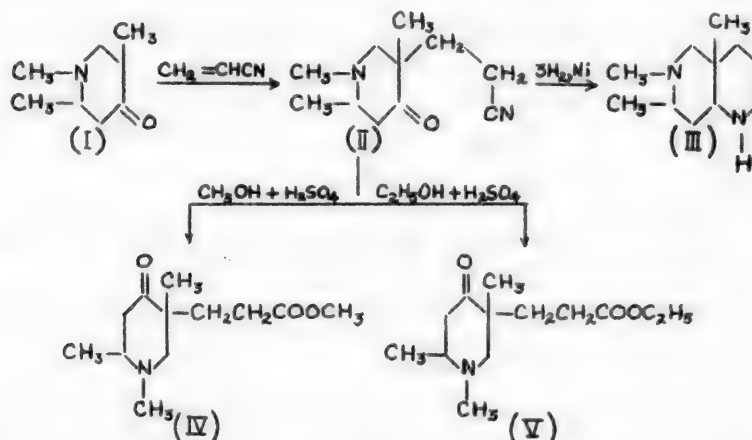
Molotov State Pedagogic Institute

CYANETHYLATION OF CYCLIC AND HETEROCYCLIC KETONES REDUCTION AND CYCLIZATION OF THE CYANETHYLATION PRODUCTS

I. N. Nazarov, G. A. Shvekhgeimer and V. A. Rudenko

In spite of the voluminous literature on the cyanethylation of various ketones, this reaction has hardly been studied at all for the heterocyclic ketones. The cyanethylation of γ -piperidones presents particular interest, since they have become readily available due to the works of our laboratory [1] and play an important role in the synthesis of valuable physiologically active compounds, in particular, of anesthetic substances.

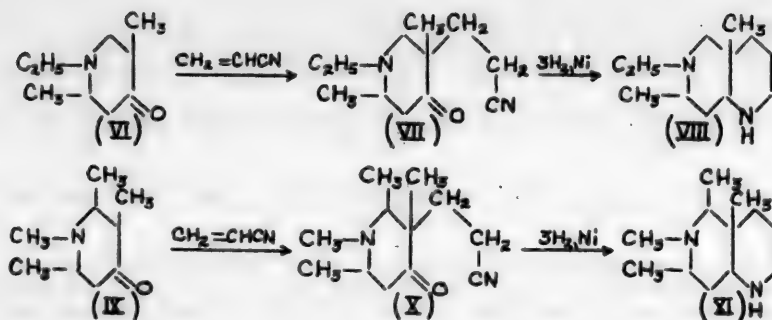
1,2,5-Trimethyl-5-(8-cyanethyl)-4-piperidone (II) was obtained in a yield of 90% by the reaction of acrylonitrile with excess 1,2,5-trimethyl-4-piperidone (I) for 24 hours at room temperature in the presence of small quantities of a 40% solution of potassium hydroxide. By hydrogenation in an autoclave at a temperature of 100° in the presence of Ni catalyst, the cyanethylated piperidone (II) was subjected to reduction cyclization, and formed trimethylperhydropyridopyridine (III) containing two condensed piperidine nuclei with an angular methyl group in a yield of 89%.



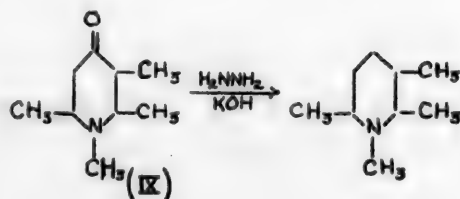
By heating the cyanethylated piperidone (II) with methyl and ethyl alcohols in the presence of sulfuric acid, the corresponding esters (IV) and (V) were obtained in a yield up to 75%.

By reaction of the cyanethylated piperidone (II) with methol alcohol a mixture of the initial cyanoketone (II) and the ketoester (IV) was obtained. Upon hydrogenation of this mixture the cyanoketone (II) was converted into the low-boiling perhydropyridopyridine (III), and after fractional distillation of the hydrogenation products the pure ketoester (IV) was successfully isolated.

Other γ -piperidones also behaved similarly in the cyanethylation reaction. Thus, for example, 1-ethyl-2,5-dimethyl-4-piperidone (VI) and 1,2,3,6-tetramethyl-4-piperidone (IX), upon cyanethylation, gave the corresponding cyanethyl derivatives (VII) and (X) in yields up to 90%, and upon hydrogenation of these last, the bicyclic compounds (VIII) and (XI) with two heterocyclic nitrogen atoms and an angular methyl group were obtained in a yield of 70-80%.



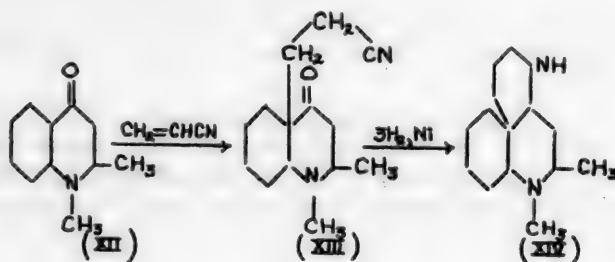
If the hydrogenation of the cyanoketone (X) is carried out at temperatures above 100° , in addition to the expected perhydropyridopyridine (XI) a considerable quantity of a low-boiling substance which corresponds in constants and analysis to piperidine with aggregate substituents amounting to C_4 . One of these piperidines could be shown to be 1,2,3,6-tetramethylpiperidine. For comparison, we obtained the latter by reduction of the 1,2,3,6-tetramethyl-4-piperidone by Kishner's method:



The thus-obtained 1,2,3,6-tetramethylpiperidine differed from the substance isolated during the hydrogenation of the cyanoketone (X), which can be explained by their different configuration.

To verify this hypothesis, the substance obtained by the hydrogenation of the cyanoketone (X) was subjected to the Kishner reaction. However, the constants of this substance after heating with potassium hydroxide again did not coincide with the constants of 1,2,3,6-tetramethylpiperidine.

The cyanethylations of polycyclic compounds containing a condensed γ -piperidone nucleus and readily obtained by the method worked out in our laboratory [1] present interesting synthetic possibilities. As an example, we accomplished the cyanethylation of 1,2-dimethyl-4-ketodecahydroquinoline (XII), during which the cyanethyl group enters into the angular position and forms the cyanethyl derivative (XIII) in a yield of 90%. Upon the hydrogenation of the latter, the tricyclic compound (XIV), containing two heterocyclic nitrogen atoms and a condensed ring in the angular position, was obtained in a yield of 81%.

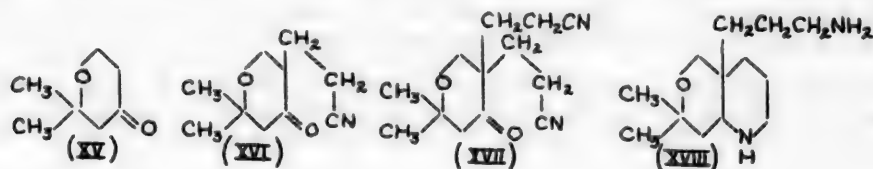


The structure of the cyanethylated ketone (XIII) was verified by a qualitative test for the formation of a formyl derivative [2] (presence of a free α -methylene group).

The angular structure of the ketone (XIII) is also a consequence of the fact that the cyclic ketones add acrylonitrile primarily to the tertiary carbon atom which has a substituent [3]. In accord with this the α -substituted cyclic ketones give high yields of monocyanethyl derivatives, while cyclic ketones which do not have substituents in the α -position readily form di- and tetracyanethylated products.

Upon the cyanethylation of 2,2-dimethyltetrahydro-4-pyrene (XV), the dicyanethyl derivative (XVII) was formed very readily, and only with a great excess of the ketone (XV) could the monocyanethylated product (XVI) be isolated successfully.

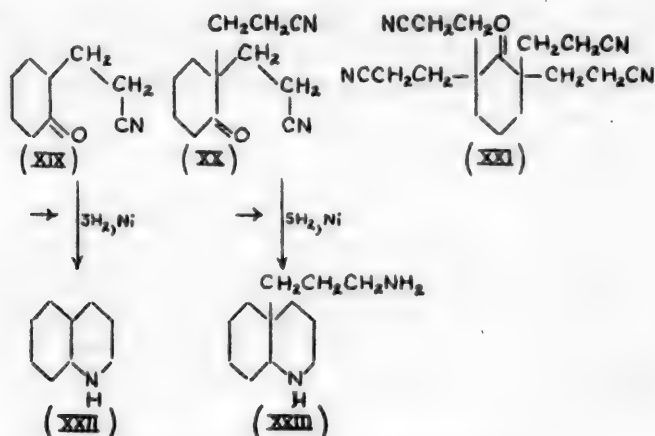
Upon the hydrogenation of the ketodinitrile (XVII) the bicyclic compound (XVIII) containing pyrane and piperidine rings was formed in a yield of 66%



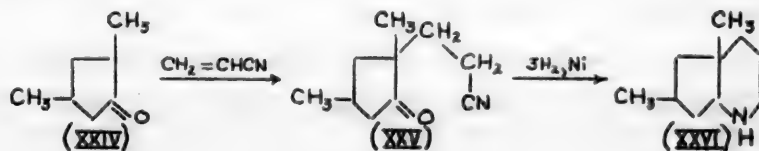
Thus, one of the two α -methylene groups in the ketone (XV) did not undergo cyanethylation; this is associated, in all probability, with the influence of the adjacent substituents (steric hindrance).

Upon the cyanethylation of cyclohexanone, as is well known, the tetracyanethyl derivative (XXI) is readily obtained, and under the conditions of excess ketone the mono- and dicyanethylated products (XIX) and (XX) were successfully isolated.

Upon the hydrogenation of the latter in the presence of Raney nickel under pressure the decahydroquinolines (XXII) and (XXIII) were obtained

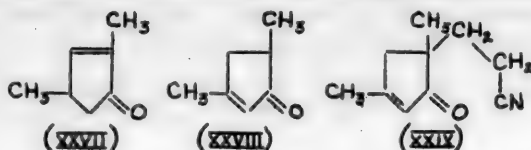


2,4-Dimethylcyclopentanone (XXIV) similarly to 2-methylcyclohexanone [4], readily adds one molecule of acrylonitrile and gives with a yield of 71% the monocyanethyl derivative (XXV). The latter is converted by hydrogenation into the perhydropyridine (XXVI) with a yield of 78%



Upon the cyanethylation of the isomeric dimethylcyclopentenones (XXVII) and (XXVIII) the same monocyanethyl derivative (XXIX), corresponding to the ketone (XXVIII), is obtained in each case. Consequently, the ketone

(XXVII) is isomerized under the conditions of the cyanethylation reaction (under the influence of alkali) into the ketone (XXVIII), as had been previously established by Nazarov and Elizarova [5].



An attempt was made to convert the unsaturated cyanoketone (XXIX) into the saturated cyanoketone (XXV) via hydrogenation of the double bond. It turned out that neither over palladium nor over platinum catalysts was the double bond in the cyanoketone (XXIX) hydrogenated under ordinary conditions.

The hydrogenation of the unsaturated cyanoketone (XXIX) in an autoclave led to the formation of the isomeric perhydropyridine (XXVI) which differs from that described above, in all probability, in its configuration.

EXPERIMENTAL

I. Reaction of Acrylonitrile With 1,2,5-Trimethyl-4-piperidone

A mixture of 50 g (0.35 mole) of 1,2,5-trimethyl-4-piperidone (I) and 3 g of a 40% aqueous solution of potassium hydroxide was placed in a three-necked flask supplied with a mechanical stirrer, a dropping funnel and a thermometer. 7 g (0.13 mole) of acrylonitrile was gradually added during energetic stirring and cooling with cold water at such a rate that the temperature of the mixture did not rise above 20°. After the addition of acrylonitrile, the stirring was continued for 6 hours at room temperature, and then the mixture was left for 48 hours. The alkali was neutralized with an equivalent quantity of concentrated hydrochloric acid, the potassium chloride which precipitated was filtered off and the filtrate was vacuum distilled.

23.1 g of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone (II) was obtained in the form of a thick yellow oil which rapidly crystallized on standing; b.p. 138-140° at 4 mm; m.p. 66.5-67.5° (from petroleum ether).

3.600 mg sub.: 0.4645 ml N₂ (19°, 738 mm). 3.380 mg sub.: 0.4400 ml N₂ (19°, 736 mm). Found %: N 14.65, 14.73. C₁₁H₁₉ON₂. Calculated %: N 14.43.

The picrate melted at 212-213° (from alcohol).

In addition, 28.4 g of the initial 1,2,5-trimethyl-4-piperidone was obtained.

The cyanethylation of the other ketones was carried out in a similar fashion (see below).

Hydrogenation of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone. 19.4 g (0.1 mole) of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone (II), 100 ml of methyl alcohol and 1 g of Raney nickel were placed in a 250 ml rotating autoclave. The hydrogenation was carried out at 100° and an initial hydrogen pressure of 100 atm. The theoretical quantity of hydrogen (6.75 liters) was absorbed in the course of 40 minutes. The mixture was cooled, the nickel filtered off and the filtrate vacuum distilled.

16.2 g of 6,7,9-trimethylperhydropyridopyridine (III) was obtained in the form of a colorless, mobile liquid with a characteristic amine odor:

B.p. 71-73.5° at 3 mm; n_D^{20} 1.4933; d_4^{20} 0.9576; M_{rD} 56.31; calculated 56.14.

2.265 mg sub.: 0.3126 ml N₂ (22°, 724 mm). 4.030 mg sub.: 0.5473 ml N₂ (20°, 723 mm). Found %: N 15.21, 15.07. C₁₁H₂₂N₂. Calculated %: N 15.38.

The picrate melted at 255-256° (from water).

The hydrogenation of the β-cyanethyl derivatives of other ketones was accomplished in an analogous fashion.

Alcoholysis of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone. a) 42 g (0.227 mole) of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone (II) was placed in a three-necked flask, supplied with a thermometer, a reflux condenser and a mechanical stirrer, and a cooled mixture of 80 ml of methyl alcohol with 45 g of concentrated sulfuric acid was added. The reaction mass was stirred for 10 hours at 74°, and after cooling was poured out into 300 ml of water. The excess sulfuric acid was neutralized with soda; the base was salted out with potash. The upper layer

was separated, while the aqueous layer was extracted with ether 5 times. The ethereal extracts were combined and dried with calcined sodium sulfate. The ether was distilled off and the residue vacuum distilled.

41.4 g of a mixture of the initial cyanoketone (II) and the piperidine ester (IV) was obtained in the form of a light yellow oil which crystallized on standing; b.p. 123-129° at 4 mm.

The cyanoketone (II) isolated from this mixture melted at 67-69° (from petroleum ether) and yielded no depression with the initial substance.

To isolate the piperidine ester (IV) in the pure form the mixture obtained was subjected to hydrogenation with the object of freeing it from the initial cyanoketone (II). 25 g of the above-described mixture of substances (II) and (IV), 100 ml of methyl alcohol and 1 g of Raney nickel were placed in a 250 ml rotating autoclave. The hydrogenation was carried out at 90-110° and the initial hydrogen pressure was 120 atm. After 1 hour 30 atm. of hydrogen had been absorbed, after which the rate of hydrogenation sharply diminished. The autoclave was cooled, the nickel filtered off, and the filtrate vacuum distilled three times.

10.5 g of trimethylperhydropyridopyridine (III) was isolated with a b.p. of 76-78° at 3.5 mm, the picrate of which melted at 255-256° and yielded no melting point depression with the sample described above.

In addition, 12.2 g of 1,2,5-trimethyl-5-(β -carbomethoxyethyl)-4-piperidone (IV) was obtained in the form of a colorless oil:

B.p. 117-119° at 5 mm; n_D^{20} 1.4703; d_4^{20} 1.0390; M_{RD} 60.99; calculated 61.02.

4.720 mg sub.: 11.030 mg CO_2 ; 3.900 mg H_2O . 5.563 mg sub.: 13.027 mg CO_2 ; 4.700 mg H_2O . Found %: C 63.77, 63.90; H 9.46, 9.42. $C_{12}H_{21}O_3N$. Calculated %: C 63.44. H 9.25.

The picrate melted at 204-205° (from water).

The ester (IV) obtained yielded an intense raspberry coloration with sodium nitroprusside in alkaline medium (test for the carbonyl group) [6].

b) A mixture of 20 g (0.1 mole) of 1,2,5-trimethyl-5-(β -cyanethyl)-4-piperidone, 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred for 20 hours at 90-92° (boiling point of the mixture). The cooling reaction mass was decomposed with 100 ml of water. The acid was neutralized with soda, the base was salted out with potash (a stable emulsion was formed), the mixture was repeatedly extracted with ether, dried with calcined sodium sulfate and vacuum distilled.

18.9 g of 1,2,5-trimethyl-5-(β -carboethoxyethyl)-4-piperidone (V) (75%) was obtained in the form of a colorless oil:

b.p. 117-118° at 3.5 mm; n_D^{20} 1.4682; d_4^{20} 1.0208; M_{RD} 65.65; calculated 65.64.

5.772 mg sub.: 0.314 ml N_2 (24°, 731 mm). 4.829 mg sub.: 0.255 ml N_2 (23°, 743 mm). Found %: N 5.99, 5.96. $C_{13}H_{23}O_3N$. Calculated %: N 5.81.

The picrate melted at 200.5-201° (from moist acetone).

II. Reaction of Acrylonitrile With 1-Ethyl-2,5-dimethyl-4-piperidone

200 g (1.3 mole) of 1-ethyl-2,5-dimethyl-4-piperidone (VI), 5 g of a 40% solution of potassium hydroxide and 20 g (0.38 mole) of acrylonitrile were taken for the reaction.

71.6 g of 1-ethyl-2,5-dimethyl-5-(β -cyanethyl)-4-piperidone (VII) was obtained in the form of a viscous yellow oil.

B.p. 155-158° at 7 mm; n_D^{20} 1.4835; d_4^{20} 1.0040; M_{RD} 59.22; calculated 59.18.

3.000 mg sub.: 0.3568 ml N_2 (21°, 735 mm). 2.880 mg sub.: 0.3438 ml N_2 (21°, 735 mm). Found %: N 13.24, 13.28. $C_{12}H_{20}ON_2$. Calculated %: N 13.46.

The picrate melted at 177-178° (from acetone).

100 g of the initial 1-ethyl-2,5-dimethyl-4-piperidone (VI) was recovered from the experiment.

Hydrogenation of 1-ethyl-2,5-dimethyl-5-(β -cyanethyl)-4-piperidone. 36.5 g (0.175 mole) of 1-ethyl-2,5-dimethyl-5-(β -cyanethyl)-4-piperidone (VII), 115 g of methyl alcohol and 2 g of Raney nickel were taken. The hydrogenation was carried out at 80-95° and an initial hydrogen pressure of 140 atm. The theoretical quantity of hydrogen (11.8 liters) was absorbed in the course of 1.5 hour.

25 g of 6-ethyl-7,9-dimethylperhydropyridopyridine (VIII) was obtained; it consisted of a colorless oil with a characteristic amine odor:

b.p. 90-94° at 5 mm; n_D^{20} 1.4917; d_4^{20} 0.9464; MR_D 60.05; calculated 60.41.

4.425 mg sub.: 0.5528 ml N_2 (22°, 724 mm). 5.235 mg sub.: 0.6697 ml N_2 (23°, 723 mm). Found %: N 14.21, 14.04. $C_{12}H_{14}N_2$. Calculated %: N 14.28.

The hydrochloride with a m.p. of 211.5-212° (from alcohol) was obtained.

III. Reaction of Acrylonitrile With 1,2,3,6-Tetramethyl-4-piperidone

135 g (0.87 mole) of 1,2,3,6-tetramethyl-4-piperidone (IX), 9 g of a 40% aqueous solution of potassium hydroxide and 15 g (0.28 mole) of acrylonitrile were taken in the reaction. After the addition of acrylonitrile, the mixture was heated for 1 hour at 70-75° and then was left for 48 hours.

42 g of 1,2,3,6-tetramethyl-3-(β -cyanethyl)-4-piperidone (X) was obtained in the form of a thick yellow oil:

b.p. 142-145° at 1 mm; n_D^{20} 1.4852; d_4^{20} 1.0183; MR_D 58.56; calculated 58.50.

3.450 mg sub.: 0.4158 ml N_2 (20°, 723 mm). 4.230 mg sub.: 0.5214 ml N_2 (20°, 718 mm). Found %: N 13.35, 13.57. $C_{12}H_{20}ON_2$. Calculated %: N 13.46.

The picrate melted at 196-197° (from acetone).

92.5 g of the initial 1,2,3,6-tetramethyl-4-piperidone (IX) was recovered from the experiment.

Hydrogenation of 1,2,3,6-tetramethyl-3-(β -cyanethyl)-4-piperidone. a) 22 g (0.105 mole) of 1,2,3,6-tetramethyl-3-(β -cyanethyl)-4-piperidone (X), 130 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 85-90° and an initial hydrogen pressure of 110 atm. The theoretical quantity of hydrogen (7.1 liters) was absorbed in the course of 30 minutes.

17 g of 6,7,8,9-tetramethylperhydropyridopyridine (XI), a colorless liquid with a characteristic amine odor, was obtained:

b.p. 97-101° at 4 mm; n_D^{20} 1.4988; d_4^{20} 0.9622; MR_D 60.76; calculated 60.41.

2.915 mg sub.: 0.3695 ml N_2 (23°, 272 mm). 4.115 mg sub.: 0.5282 ml N_2 (24°, 716 mm). Found %: N 13.98, 14.09. $C_{12}H_{24}N_2$. Calculated %: N 14.28.

The hydrochloride melted at 140-142.5°.

In addition, 1.1 g of a substance with a b.p. of 58-60° at 11 mm; n_D^{20} 1.4553 was obtained (see below).

b) 12.5 g (0.06 mole) of the ketonitrile (X), 100 ml of methyl alcohol and 1 g of Raney nickel were taken. The hydrogenation was carried out at 100-120° and an initial hydrogen pressure of 120 atm. 54 atm of hydrogen was absorbed in the course of 1 hour (30 atm was theoretically required for the reduction cyclization).

3.5 g of the above described 6,7,8,9-tetramethylperhydropyridopyridine (XI) with a b.p. of 122-125° at 10 mm; n_D^{20} 1.4989 was obtained.

In addition, 4.9 g of a substance agreeing in analysis with 1,2,3,6-tetramethylpiperidine was obtained in the form of a colorless, mobile liquid with a sharp amine odor:

b.p. 32-33° at 3 mm; 184-189° at 761 mm; n_D^{20} 1.4549; d_4^{20} 0.8506.

5.760 mg sub.: 0.4792 ml N_2 (18°, 743 mm). 4.635 mg sub.: 0.3911 ml N_2 (19°, 743 mm). 3.670 mg sub.: 0.3273 ml N_2 (23°, 729 mm). Found %: N 9.54, 9.64, 9.86. $C_9H_{19}N$. Calculated %: N 9.93.

The hydrochloride melted at 145-146° (from acetone). The picrate was not successfully isolated in the crystalline form.

By heating this substance (3 g) with potassium hydroxide in 1,3-butylene glycol for 5.5 hours at 150-160° (under the conditions of Kizhner's reduction; see below), 2.1 g of base with a b.p. of 172-176° at 748 mm was obtained; its hydrochloride also melted at 145-146° and yielded no melting point depression with the preceding sample.

The picrate was not successfully isolated in the crystalline form.

Reduction of 1,2,3,6-tetramethyl-4-piperidone by Kizhner's method. A mixture of 15.5 g (0.1 mole) of 1,2,3,6-tetramethyl-4-piperidone (XI), 75 ml of 1,3-butylene glycol, 18 g of powdered potassium hydroxide and 15 g of hydrazine hydrate was heated with a reflux condenser for 2.5 hours at 148-150°. An energetic evolution of gas bubbles and a darkening of the mixture were observed. After this the reflux condenser was replaced by a headpiece in which a thermometer was placed so that the bulb was deeply immersed in the liquid. The lead off of the headpiece was joined with a straight condenser and a small quantity of liquid was distilled off at a temperature of 180°. Then the headpiece was replaced by the reflux condenser and the mixture was heated for 3 hours at 180-195°. The mixture was cooled, the reflux condenser was again replaced by the headpiece and all the substance was distilled off which boiled below 190°. Both distillates were combined and saturated with potash; the upper layer was separated while the lower layer was twice extracted with ether.

The product was dried with fused sodium hydroxide and distilled. 9.3 g (66%) of 1,2,3,6-tetramethylpiperidine was obtained; it consisted of a colorless, mobile liquid with a sharp piperidine odor:

b.p. 161-163° at 748 mm; 48-49.5° at 11 mm; n_D^{20} 1.4531; d_4^{20} 0.8407; MR_D 45.34; calculated 45.50.

3.395 mg sub.: 0.289 ml N_2 (22°, 757 mm). 3.115 mg sub.: 0.269 ml N_2 (22°, 758 mm). Found %: N 9.77, 9.98. $C_9H_{19}N$. Calculated %: N 9.93.

The picrate with a m.p. of 210.5-211° (from alcohol) was obtained. The hydrochloride could not be obtained in the crystalline form.

IV. Reaction of Acrylonitrile With 1,2-Dimethyldecahydro-4-quinolone

38 g (0.210 mole) of 1,2-dimethyldecahydro-4-quinolone (XII), 1.2 g of a 40% aqueous solution of potassium hydroxide and 3.5 g (0.066 mole) of acrylonitrile were taken.

14 g of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone (XIII) was obtained; it consisted of a light orange, viscous oil; b.p. 166-170° at 2 mm; n_D^{20} 1.5069, d_4^{20} 1.0608; MR_D 65.63; calculated 66.22.

6.419 mg sub.: 0.684 ml N_2 (18°, 751 mm). 6.510 mg sub.: 0.711 ml N_2 (20°, 744 mm). Found %: N 12.20, 12.35. $C_{14}H_{22}ON_2$. Calculated %: N 11.96.

The picrate melted at 197-197.5° (from a mixture of moist acetone and alcohol).

15.9 g of the initial 1,2-dimethyldecahydro-4-quinolone (XII) was recovered from the experiment.

Hydrogenation of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone. 15 g (0.064 mole) of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone (XIII), 135 ml of methyl alcohol and 1 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 100 atm. The theoretical quantity of hydrogen (4.3 liters) was absorbed in the course of 30 minutes.

12.4 g of a substance (XIV) was obtained in the form of a colorless, viscous oil with a characteristic amine odor:

b.p. 134-138° at 5 mm; n_D^{20} 1.5262; d_4^{20} 1.0360; MR_D 65.80; calculated 66.69.

2.620 mg sub.: 0.3047 ml N_2 (24°, 729 mm). 3.695 mg sub.: 0.4282 ml N_2 (23°, 729 mm). Found %: N 12.84, 12.84. $C_{14}H_{26}N_2$. Calculated %: N 12.61.

The hydrochloride with a m.p. of 221-222° (from alcohol) was obtained.

Reaction of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone with benzaldehyde. 2.4 g (0.01 mole) of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone (XIII) was dissolved in 10 ml of ethyl alcohol. 4 ml of a 15% aqueous solution of sodium hydroxide, 1.2 ml of freshly prepared benzaldehyde and 1 ml of water were added to the solution. The solution became completely transparent while being stirred. After 15 minutes, the evolution of an oil began, which did not crystallize on standing even for a month. 1.3 g of a thick yellow oil was obtained by distillation, which did not crystallize on standing:

b.p. 135-195° (the bulk at 190-195°) at 0.015 mm.

Reaction of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone with ethyl formate. 0.23 g (0.01 mole) of finely divided metallic sodium, 2.34 g (0.01 mole) of 1,2-dimethyl-10-(β -cyanethyl)-decahydro-4-quinolone (XIII) and 30 ml of absolute ether were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a dropping funnel. 1.2 g (0.016 mole) of ethyl formate was added to the stirred mixture. The evolution of bubbles of gas was observed. The mixture was stirred for 3 hours and then left overnight. A brown precipitate

settled out. The formylation product was not isolated, but was used for a qualitative reaction for a 1,3-dicarbonyl compound.

Qualitative test for a 1,3-dicarbonyl compounds [2]. 1.45 g (0.01 mole) of phenylhydrazine hydrochloride in 30 ml of water was gradually added to the formylation product while it was being stirred; the mixture evolved an appreciable amount of heat. After the spontaneous heat evolution of the mixture was ended, the ethereal layer was separated while the aqueous layer was twice extracted with ether. The ether was distilled off, the residue dissolved in 15 ml of ethyl alcohol. The alcoholic solution was placed in a round-bottomed flask, joined with a reflux condenser, and the mixture was heated to boiling. 1.15 g (0.05 mole) of metallic sodium was gradually added to the boiling alcoholic solution. After solution of all the sodium the mixture was cooled and 30 ml of water was added. The alcohol was distilled off in a vacuum; an oil thereupon precipitated which was extracted three times with ether. The ether was distilled off and the residue dissolved in 10 ml of concentrated sulfuric acid. The solution obtained, when shaken with an aqueous solution of sodium nitrite, yielded a cherry red color and, on shaking with an aqueous solution of potassium bichromate, exhibited a blue-green coloration.

V. Reaction of Acrylonitrile With 2,4-Dimethylcyclopentanone

110 g (1 mole) of 2,4-dimethylcyclopentanone (XXIV) (b.p. 74-76° at 45 mm; n_D^{20} 1.4319), 8 g of a 40% aqueous solution of potassium hydroxide and 20 g (0.38 mole) of acrylonitrile were taken.

44 g of 2,4-dimethyl-2-(β -cyanethyl)-cyclopentanone (XXV) was obtained in the form of a colorless oil:

b.p. 109.5-110° at 3.5 mm; n_D^{20} 1.4617; d_4^{20} 0.9851; MR_D 46.02; calculated 46.01.

5.690 mg sub.: 0.421 ml N_2 (20°, 749 mm). 9.055 mg sub.: 0.677 ml N_2 (20°, 749 mm). Found %: N 8.49, 8.38. $C_{11}H_{15}ON$. Calculated %: N 8.48.

72.8 g of the initial 2,4-dimethylcyclopentanone (b.p. 71-73° at 43 mm; n_D^{20} 1.4316) was recovered from the experiment.

Hydrogenation of 2,4-dimethyl-2-(β -cyanethyl)-cyclopentanone. 25 g (0.15 mole) of 2,4-dimethyl-2-(β -cyanethyl)-cyclopentanone (XXV), 100 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (10 liters) was absorbed in the course of 45 minutes.

18 g of 4a,6-dimethylperhydropyridine (XXVI) was obtained; it consisted of a colorless, mobile liquid with a sharp amine odor:

b.p. 67-69° at 8 mm; n_D^{20} 1.4751; d_4^{20} 0.8975; MR_D 48.00; calculated 47.58.

5.720 mg sub.: 0.455 ml N_2 (18°, 753 mm). 7.285 mg sub.: 0.591 ml N_2 (22°, 744 mm). Found %: N 9.20, 9.20. $C_{10}H_{13}N$. Calculated %: N 9.15.

The hydrochloride with a m.p. of 143-144° (from acetone) was obtained.

VI. Reaction of Acrylonitrile With 2,4-Dimethyl- Δ^4 -cyclopentenone

70 g (0.64 mole) of 2,4-dimethyl- Δ^4 -cyclopentenone (XXVII), 5 g of a 40% aqueous solution of potassium hydroxide and 35 g (0.66 mole) of acrylonitrile were taken in the reaction.

25.1 g of 2,4-dimethyl-2-(β -cyanethyl)- Δ^4 -cyclopentenone (XXIX) was obtained in the form of a colorless viscous oil:

b.p. 118-122° at 5.5 mm; n_D^{20} 1.4760; d_4^{20} 1.0353; MR_D 44.46; calculated 45.54; EMR_D 1.08.

6.515 mg sub.: 1.97 ml (0.02 N hyposulfite). 10.358 mg sub.: 3.15 ml (0.02 N hyposulfite). Found %: N 8.55; 8.59. $C_{10}H_{13}ON$. Calculated %: N 8.59.

2,4-Dinitrophenylhydrazone melted at 109.5-111° (from methanol).

28 g of the initial 2,4-dimethyl- Δ^4 -cyclopentenone (b.p. 179-182°; n_D^{20} 1.4758) was recovered from the experiment.

The substance obtained did not appear to be homogeneous. On shaking it with hydrogen in the presence of Pd- and Pt catalysts, hydrogenation did not occur, but after distillation, a pure substance was isolated:

b.p. 110.5-111° at 4.5 mm; n_D^{20} 1.4759; d_4^{20} 1.0834; MR_D 44.48; calculated 45.54; EMR_D 1.06.

3.545 mg sub.: 9.447 mg CO₂; 2.585 mg H₂O. 4.510 mg sub.: 12.027 mg CO₂; 3.305 mg H₂O. Found %: C 72.72, 72.77; H 8.11, 8.20. C₁₀H₁₃ON. Calculated %: C 73.62; H 7.97.

The 2,4-dinitrophenylhydrazone of this cyanoketone melted at 162.5-164°, and then solidified and again melted at 176-179° (from methanol).

Hydrogenation of 2,4-dimethyl-2-(β-cyanethyl)-Δ⁴-cyclopentenone. 20 g (0.12 mole) of 2,4-dimethyl-2-(β-cyanethyl)-Δ⁴-cyclopentenone (XXIX), 100 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 90-110° and the initial hydrogen pressure was 125 atm. The theoretical quantity of hydrogen (10.8 liters) was absorbed in the course of 2 hours.

4.5 g of the isomeric 4a,6-dimethylperhydropyridine (XXVI) was obtained; it consisted of a colorless, mobile liquid with a sharp amine odor:

b.p. 69-71° at 9 mm; n_D²⁰ 1.4757; d₄²⁰ 0.9083; MR_D 47.48; calculated 47.58.

4.090 mg sub.: 0.3215 ml N₂ (19°, 741 mm). 3.280 mg sub.: 0.2617 ml N₂ (19°, 741 mm). Found %: N 8.93, 9.09. C₁₀H₁₃N. Calculated %: N 9.15.

The hydrochloride was prepared and had a m.p. of 226-227° (from an acetone alcohol mixture).

VII. Reaction of Acrylonitrile With 2,4-Dimethyl-Δ²-cyclopentenone

83 g (0.75 mole) of 2,4-dimethyl-Δ²-cyclopentenone (XXVIII) (b.p. 48-50° at 8 mm; n_D²⁰ 1.4664), 2 g of a 40% aqueous solution of potassium hydroxide and 15 g (0.28 mole) of acrylonitrile were taken in the reaction. The reaction was carried out for 8 hours at a temperature of 20-30°.

5.5 g of 2,4-dimethyl-2-(β-cyanethyl)-Δ⁴-cyclopentenone (XXIX) was obtained in the form of a thick colorless oil:

b.p. 110-117° at 3.5 mm; n_D²⁰ 1.4768; d₄²⁰ 1.0345; MR_D 44.71; calculated 45.54; EMR_D 0.83.

The 2,4-dinitrophenylhydrazone melted at 178-180° (from methanol) and gave no melting point depression with the preceding sample.

68 g of the initial 2,4-dimethyl-Δ²-cyclopentenone (b.p. 48-49° at 8 mm; n_D²⁰ 1.4659) was recovered from the experiment.

VIII. Reaction of Acrylonitrile With 2,2-Dimethyltetrahydro-4-pyrone

a) 185 g (1.445 mole) of 2,2-dimethyltetrahydro-4-pyrone (XV), 12 g of a 40% aqueous solution of potassium hydroxide and 20 g (0.38 mole) of acrylonitrile were taken in the reaction.

17.8 g of monocyanethylated 2,2-dimethyltetrahydro-4-pyrone (XVI) was obtained; it consisted of a thick, light yellow oil:

b.p. 132-136° at 5 mm; 124-126° at 4 mm; n_D²⁰ 1.4735; d₄²⁰ 1.0601; MR_D 47.94; calculated 47.65.

11.20 mg sub.: 27.36 mg CO₂; 8.76 mg H₂O. 10.71 mg sub.: 26.07 mg CO₂; 8.35 mg H₂O. Found %: C 66.66, 66.43; H 8.75, 8.71. C₁₀H₁₅O₂N. Calculated %: C 66.30; H 8.29.

In addition, 44.7 g of dicyanethylated 2,2-dimethyltetrahydro-4-pyrone (XVII) was obtained; it consisted of a crystalline white mass, m.p. 105.5-106.5° (from alcohol).

4.495 mg sub.: 0.470 ml N₂ (20°, 760 mm). 5.139 mg sub.: 0.633 ml N₂ (20°, 760 mm). Found %: N 12.18, 12.11. C₁₃H₁₉O₂N₂. Calculated %: N 11.96.

b) 117 g (0.9 mole) of the ketone (XV), 15 g of a 40% aqueous potassium hydroxide solution, 96 g (1.8 mole) of acrylonitrile and 100 ml of dioxane were taken in the reaction.

161 g of dicyanethylated product (XVII) with a m.p. of 103.5-105.5° (from alcohol) was obtained. A mixed sample with the substance obtained from experiment a) yielded no depression.

Hydrogenation of 2,2-dimethyl-5,5-di(β-cyanethyl)-tetrahydro-4-pyrone. 23.4 g (0.1 mole) of 2,2-dimethyl-5,5-di(β-cyanethyl)-tetrahydro-4-pyrone (XVII), 100 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 90-110° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (11.2 liters) was absorbed in the course of 2 hours.

15.1 g of 7,7-dimethyl-9-(γ -aminopropyl)-perhydropyranopyridine (XVIII) was obtained; it consisted of a colorless viscous oil:

b.p. 130-134° at 4 mm; n_D^{20} 1.5149; d_4^{20} 1.0637; MR_D 64.06; calculated 66.50.

4.490 mg sub.: 0.4784 ml N_2 (19°, 735 mm). 5.085 mg sub.: 0.5499 ml N_2 (20°, 732 mm). Found %: N 12.07, 12.13. $C_{15}H_{25}ON_2$. Calculated %: N 12.34.

The hydrochloride, which melted at 229.5-231° with decomposition (from acetone) was obtained.

IX. Reaction of Acrylonitrile with Cyclohexanone

400 g (4 moles) of cyclohexanone, 30 g of a 40% aqueous potassium hydroxide solution and 106 g (2 moles) of acrylonitrile were taken in the reaction. The following fractions were obtained:

1) 2-(β -Cyanethyl)-cyclohexanone (XIX)-89 g, b.p. 127-129° at 8 mm [7]; 2) 2,2-di(β -cyanethyl)-cyclohexanone (XX)-54 g, b.p. 185-192° at 0.1 mm, m.p. 68-69° (from alcohol) [7].

38 g of crystalline tetra(β -cyanethyl)-cyclohexanone (XXI) was isolated from the residue; m.p. 164-165.5° (from a mixture of alcohol and acetone [7]).

243 g of cyclohexanone was recovered from the experiment.

Hydrogenation of 2-(β -cyanethyl)-cyclohexanone. 30.2 g (0.2 mole) of 2-(β -cyanethyl)-cyclohexanone (XIX), 100 ml of methyl alcohol and 2 g of Raney nickel were taken. Hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (13.5 liters) was absorbed in the course of 1 hour.

19 g of the previously described [8] decahydroquinoline (XXII) with a b.p. of 74-75° at 9 mm; 204-205° at 756 mm; n_D^{20} 1.4927 was evolved.

The hydrochloride with a m.p. of 231.5-233° (from a mixture of acetone and alcohol) [8] was obtained.

Hydrogenation of 2,2-di(β -cyanethyl)-cyclohexanone. 20.4 g (0.1 mole) of 2,2-di(β -cyanethyl)-cyclohexanone (XX), 100 ml of methyl alcohol and 1 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 150 atm. The theoretical quantity of hydrogen (11.2 liters) was absorbed in the course of 45 minutes.

8.1 g of 10-(γ -aminopropyl)-decahydroquinoline (XXIII) was obtained; it consisted of a white crystalline mass with an amine odor; b.p. 114-120° at 4 mm; m.p. 42-43°. The hydrochloride with a m.p. of 296-298° (from moist alcohol) was prepared.

4.870 mg sub.: 0.431 ml N_2 (20°, 755 mm). 4.450 mg sub.: 0.394 ml N_2 (20°, 752 mm). Found %: N 10.28, 10.20. $C_{12}H_{20}N_2Cl_2$. Calculated %: N 10.40.

The picrate with a m.p. of 188.5-189.5° (from methyl alcohol) was prepared.

SUMMARY

1. The cyanethylation reaction was carried out with the following cyclic and heterocyclic ketones: cyclohexanone, 2,4-dimethylcyclopentanone, 2,4-dimethyl- Δ^4 -cyclopentenone, 2,4-dimethyl- Δ^2 -cyclopentenone, 2,2-dimethyl tetrahydro-4-pyrone, 1,2,5-trimethyl-4-piperidone, 1,2,3,6-tetramethyl-4-piperidone, 1-ethyl-2,5-dimethyl-4-piperidone and 1,2-dimethyldecahydro-4-quinolone.

2. The ketones which have a substituent in the α -position: 2,4-dimethylcyclopentanone, 1,2,5-trimethyl-4-piperidone, 1,2,3,6-tetramethyl-4-piperidone, 1-ethyl-2,5-dimethyl-4-piperidone and 1,2-dimethyldecahydro-4-quinolone form monocyanethyl products in high yields; 2,2-dimethyltetrahydro-4-pyrone primarily forms a di-cyanethylated product.

3. The same ketonitrile was obtained from 2,4-dimethyl- Δ^4 -cyclopentenone and 2,4- Δ^2 -cyclopentenone.

4. The ketonitriles and ketodinitriles obtained are cyclized by hydrogenation in an autoclave into the corresponding piperidine systems. The hydrogenation of 1,2,3,6-tetramethyl-3-(β -cyanethyl)-4-piperidone is accompanied by hydrogenolysis at temperatures above 100°.

5. The expected 1,2,5-trimethyl-5-(β -carboalkoxyethyl)-4-piperidones are formed in yields up to 75% by the alcoholysis of 1,2,5-trimethyl-5-(β -cyanethyl)-4-piperidone in methyl and ethyl alcohols.

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HYDROLYSIS, ALCOHOLYSIS AND HYDROGENATION OF

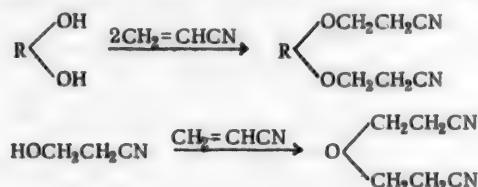
β -CYANETHYL ETHERS OF GLYCOLS

I. N. Nazarov, G. A. Shvekhgeimer and V. A. Rudenko

The addition reaction of acrylonitrile to substances having a "mobile" hydrogen atom (cyanethylation reaction), has acquired enormous significance for synthetic organic chemistry in the last few years. Introduction of the nitrile group gives rich possibilities for the synthesis of various classes of organic compounds. This explains the exceptionally great interest in the cyanethylation reaction, to the study of which numerous experimental works and also a number of literature reviews published in the course of the last five years [1] have been devoted.

Many valuable substances, which have found wide practical application, have been synthesized with the aid of the cyanethylation reaction. The addition products of acrylonitrile to glycols and ethylenecyanhydrin are particularly interesting. The di-(β -cyanethyl) ethers thus obtained are the starting materials for the synthesis of the corresponding diamines, dicarboxylic acids and their esters with oxygen heteroatoms in the basic carbon chain. These diamines, dicarboxylic acids and their esters can be used as intermediate products for the preparation of new synthetic fibers with increased hydrophilic qualities, plastics, and other valuable products.

The cyanethylation of glycols and of ethylene cyanhydrin has been quite well studied [1, 8]. This reaction proceeds readily with high yields under the action of alkaline catalysts



However, the further conversions of the di-(β -cyanethyl) ethers obtained have been insufficiently studied.

Alkaline hydrolysis was unsuitable for the saponification of the β -cyanethyl ethers into the corresponding carboxylic acids, in view of the fact that the addition products of acrylonitrile to alcohols and glycols are decomposed into the initial components by heating in the presence of alkali (reversibility of the cyanethylation reaction). Saponification of the β -cyanethyl ethers with the aid of concentrated hydrochloric acid [2] was, therefore, proposed.

The alcoholysis of the addition products of acrylonitrile to alcohols and glycols has hardly been described in the literature, with the exception of isolated patent data [3, 4], in which neither the conditions under which the reaction was carried out nor the yields of the ethers obtained were set forth.

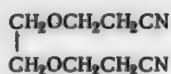
The hydrogenation of β -cyanethyl ethers into the corresponding amines has been just as little studied. Only the hydrogenation of alkyl- β -cyanethyl ethers [5] and of the di-(β -cyanethyl) ether [6] has been described in the literature.

Relative to the hydrogenation of di-(β -cyanethyl) ethers of glycols there are only very brief patent instructions [7] in the literature.

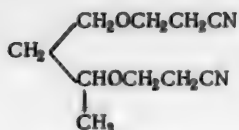
We carried out the cyanethylation of glycols and ethylene cyanhydrin in the presence of a 40% aqueous potassium hydroxide solution as had been described by Bruson [8]. The corresponding di-(β -cyanethyl) ether (I) was obtained in a yield of 96% by the cyanethylation of ethylene glycol. The di-(β -cyanethyl) ether (II) was obtained in a yield of 92% by the cyanethylation of 1,3-butylene glycol. We obtained the crystalline di-(β -cyanethyl) ether of 1,4-butylene glycol (III) which had not been described in the literature. Yield 90%.

Acrylonitrile adds to diethylene glycol in the presence of a 40% aqueous solution of potassium hydroxide with the formation of di-(β -cyanethyl) ether (IV) in a yield of 97%.

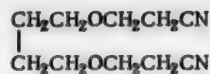
The di-(β -cyanethyl) ether (V) was obtained in a yield of 92% by the addition of acrylonitrile to ethylene cyanhydrin.



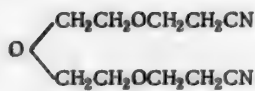
(I)



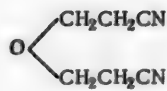
(II)



(III)



(IV)



(V)

The hydrolysis of the di-(β -cyanethyl) ethers (I-V) was carried out by the method of Christian and Hixon [2] by heating with concentrated hydrochloric acid. The yields and the constants of the thereby-obtained dicarboxylic acids (VI-X) are indicated in Table 1.

TABLE 1

Formula	M.p. (in °)	Yield (in %)
(VI) $\begin{array}{c} \text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \end{array}$	65-66	92
(VII) $\begin{array}{c} \text{CH}_3\text{CHOCH}_2\text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \end{array}$	Oil	90
(VIII) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \end{array}$	90	95
(IX) $\begin{array}{c} \text{O} \begin{cases} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \end{cases} \end{array}$	Oil	90
(X) $\begin{array}{c} \text{O} \begin{cases} \text{CH}_2\text{CH}_2\text{COOH} \\ \text{CH}_2\text{CH}_2\text{COOH} \end{cases} \end{array}$	60-61	97

The conversion of the di-(β -cyanethyl) ethers (I-V) into esters of the corresponding dicarboxylic acids (XI-XX) was accomplished via heating the nitriles with alcohols in the presence of concentrated sulfuric acid. In each case, both ethyl and methyl alcohols were used. The results of the experiments are set forth in Table 2.

We also accomplished the conversion of the di-(β -cyanethyl) ethers (I-V) into the diamines (XXI-XXV) via catalytic hydrogenation (over Raney nickel) in methyl alcohol saturated with dry ammonia (to suppress the formation of secondary amines). The hydrogenation proceeds rapidly at temperatures of 90-110° and an initial hydrogen pressure of 80-150 atm. The yields and constants of the diamines obtained are set forth in Table 3.

The diamines, dicarboxylic acids and their esters described in this paper can be employed to prepare new polyamide resins which contain oxygen heteroatoms in the chain and are distinguished by increased hydrophilic qualities.

EXPERIMENTAL

I. Reaction of Acrylonitrile with Ethylene Glycol

744 g (12 moles) of ethylene glycol and 75 g of a 40% aqueous solution of potassium hydroxide were placed in a three-necked flask supplied with a mechanical stirrer, a dropping funnel and a thermometer. 1272 g (24 moles) of acrylonitrile was added over a period of 6 hours while the mixture was being energetically stirred and cooled with cold water. The temperature of the mixture should not rise above 30°. After the addition of all the acrylonitrile the mixture was stirred at room temperature for 4 hours and left overnight. On the next day, the alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off, and the filtrate was vacuum distilled. 1957 g of the di-(β -cyanethyl) ether of ethylene glycol (I) was obtained:

b.p. 160-169° at 2 mm; n_D^{20} 1.4495 [8].

The experiments described below which involved the cyanethylation of other glycols were carried out in the same way.

Hydrolysis of the Di-(β -cyanethyl) Ether of Ethylene Glycol

450 g (2.7 moles) of the di-(β -cyanethyl) ether of ethylene glycol (I) was placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a thermometer. 1000 ml of concentrated hydrochloric acid was gradually added over a period of 1 hour while the mixture was being cooled and stirred. After the temperature of the mixture ceased to rise spontaneously, the stirring was continued for 3 hours at 70-80° and for 40 minutes at 95-98°. The reaction mass was cooled, the ammonium chloride which precipitated was filtered off and the water was distilled off from the filtrate in a vacuum. The residue was extracted with warm acetone, the extract

TABLE 2

Formula	Yield (in %)	B. p. (in °) at a pressure (in mm)	n_D^{20}	d_4^{20}	MRD	
					found	calculated
(XI) $\begin{array}{c} \text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \\ \\ \text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \end{array}$	48	136 (4), m.p. 28.5-29°	—	—	—	—
(XII) $\begin{array}{c} \text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	68	135-137 (2.5)	1.4361	1.0654	64.31	64.21
(XIII) $\begin{array}{c} \text{CH}_3\text{CHOCH}_2\text{CH}_2\text{COOCH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \end{array}$	64.5	135-137 (3.5)	1.4368	1.0662	64.25	64.21
(XIV) $\begin{array}{c} \text{CH}_3\text{CHOCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	71	141-143 (3)	1.4359	1.0292	73.65	73.45
(XV) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \end{array}$	64	146-148 (4)	1.4389	1.0691	64.41	64.21
(XVI) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	66	154-155 (4)	1.4380	1.0329	73.70	73.45
(XVII) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOCH}_3 \end{array}$	72	152-157 (3)	1.4429	1.1161	66.11	65.85
(XVIII) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	72	167-169 (4)	1.4395	1.0726	75.11	75.09
(XIX) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{COOCH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{COOCH}_3 \end{array}$	54	94-96 (4)	1.4288	1.1127	44.01	44.09
(XX) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	53	124-125 (7) 104-106 (4)	1.4274	1.0036	53.24	53.33

TABLE 3

Formula	Yield (in %)	B. p. (in °) at a pressure (in mm)	n_D^{20}	d_4^{20}	MRD	
					found	calculated
(XXI) $\begin{array}{c} \text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$	85	113-115 (4)	1.4638	0.9835	49.34	49.27
(XXII) $\begin{array}{c} \text{CH}_3-\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$	79	136-139 (6)	1.4621	0.9501	58.75	58.51
(XXIII) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$	90	134-137 (3)	1.4619	0.9624	58.55	58.51
(XXIV) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$	81	146-148 (4)	1.4642	1.0107	60.08	60.15
(XXV) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$	76	72 (4)	1.4595	—	—	—

was filtered free of ammonium chloride, and the acetone was distilled off. The residue crystallized on standing, 507 g of the dicarboxylic acid (VI) was obtained with a m.p. of 65-66° (from a benzene-acetone mixture).

The hydrolysis of the other β -cyanethyl ethers was accomplished analogously (see below).

Hydrogenation of the Di-(β -cyanethyl) Ether of Ethylene Glycol

A 2.5 liter rotating autoclave was charged with 250 g (1.5 mole) of the di-(β -cyanethyl) ether of ethylene glycol, 600 ml of methyl alcohol saturated with dry ammonia, and 15 g of Raney nickel. The hydrogenation was carried out at 100-110° for 1 hour at an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (130 liters) was absorbed, 224 g of the di-(γ -aminopropyl) ether of ethylene glycol (XXI) was obtained:

b.p. 113-115° at 4 mm; n_D^{20} 1.4638; d_4^{20} 0.9835; MR_D 49.34; calculated 49.27.

3.538 mg sub.: 0.489 ml N_2 (20°, 754 mm). 5.903 mg sub.: 0.825 ml N_2 (22°, 745 mm). Found %: N 15.97, 15.86. $C_8H_{13}O_2N_2$. Calculated %: N 15.90.

The phenylcarbamide with a m.p. of 146-147° (from alcohol) was obtained from the diamine and phenylisocyanate.

3.230 mg sub.: 0.4167 ml N_2 (20°, 713 mm). 2.195 mg sub.: 0.2833 ml N_2 (20°, 713 mm). Found %: N 14.10, 14.11. $C_{15}H_{15}O_3N_3$. Calculated %: N 14.24.

Alcoholysis of the Di-(β -cyanethyl) Ether of Ethylene Glycol

a) 84 g (0.5 mole) of the di-(β -cyanethyl) ether of ethylene glycol, 250 ml of methyl alcohol and 150 g of concentrated sulfuric acid were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a thermometer. The mixture was stirred for 12 hours at 80-84° (boiling point of the mixture). After this, the reaction mass was poured out into 500 ml of water, and the product was carefully extracted with ether. The ethereal extracts were combined, washed with a soda solution, dried with calcined sodium sulfate and vacuum distilled, 56.1 g of the dimethyl ester (XI) was obtained:

b.p. 136° at 4 mm; m.p. 28.5-29°.

8.115 mg sub.: 15.315 mg CO_2 ; 5.550 mg H_2O . 5.345 mg sub.: 10.108 mg CO_2 ; 3.730 mg H_2O . Found %: C 51.25, 51.61; H 7.61, 7.74. $C_{18}H_{18}O_6$. Calculated %: C 51.28; H 7.69.

The other experiments involving the alcoholysis of β -cyanethyl ethers were carried out in a similar manner.

b) A mixture of 16.8 g (0.1 mole) of the di-(β -cyanethyl) ether of ethylene glycol, 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid were stirred at 94-98° (the mixture boiled) for 8 hours. The cooled reaction mass was poured out into 100 ml of water and treated as described above. 17.8 g of the diethyl ester (XII) was obtained:

b.p. 135-137° at 2.5 mm; n_D^{20} 1.4361; d_4^{20} 1.0654; MR_D 64.31; calculated 64.21.

5.639 mg sub.: 11.410 mg CO_2 ; 4.177 mg H_2O . 7.735 mg sub.: 15.610 mg CO_2 ; 5.785 mg H_2O . Found %: C 55.22, 55.07; H 8.28, 8.37. $C_{18}H_{22}O_6$. Calculated %: C 54.97; H 8.39.

II. Reaction of Acrylonitrile With 1,3-Butylene Glycol

90 g (1 mole) of 1,3-butylene glycol, 8 g of a 40% aqueous potassium hydroxide solution and 106 g (2 moles) of acrylonitrile were taken in the reaction. 182 g of the di-(β -cyanethyl) ether of 1,3-butylene glycol (II) was obtained:

b.p. 155-165° at 0.3 mm; n_D^{20} 1.4467 [8].

Hydrogenation of the Di-(β -cyanethyl) Ether of 1,3-Butylene Glycol

19.6 g (0.1 mole) of the di-(β -cyanethyl) ether of 1,3-butylene glycol, 55 ml of methyl alcohol saturated with dry ammonia, and 2 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° for 1 hour and 20 minutes at an initial hydrogen pressure of 95 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed. 16.2 g of the di-(γ -aminopropyl) ether of 1,3-butylene glycol (XXII) was obtained:

b.p. 136-139° at 6 mm; n_D^{20} 1.4621; d_4^{20} 0.9595; MR_D 58.76; calculated 58.51.

2.588 mg sub.: 0.300 ml N_2 (19°, 749 mm). 3.684 mg sub.: 0.435 ml N_2 (19°, 749 mm). Found %: N 13.36, 13.60. $C_{10}H_{24}O_2N_2$. Calculated %: N 13.72.

Hydrolysis of the Di-(β -cyanethyl) Ether of 1,3-Butylene Glycol

A mixture of 19.6 g (0.1 mole) of di-(β -cyanoethyl) ether of 1,3-butylene glycol in 50 ml of concentrated hydrochloric acid was stirred at 70-80° for one hour and at 95° for 45 minutes. 21.1 g of the dicarboxylic acid (VIII) was obtained, in the form of a yellow, noncrystallizing oil.

Alcoholysis of the Di-(β -cyanethyl) Ether of 1,3-Butylene Glycol

a) A mixture of 19.6 g (0.1 mole) of the di-(β -cyanethyl) ether of 1,3-butylene glycol, 55 ml of methyl alcohol and 30 g of concentrated sulfuric acid was stirred at 90-94° (the mixture boiled) for 6 hours. 16.9 g of the dimethyl ester (XIII) was obtained:

b.p. 135-137° at 3.5 mm; n_D^{20} 1.4368; d_4^{20} 1.0662; MR_D 64.25; calculated 64.21.

5.390 mg sub.: 10.880 mg CO₂; 4.076 mg H₂O. 4.982 mg sub.: 10.092 mg CO₂; 3.798 mg H₂O. Found %: C 55.09, 55.28; H 8.46, 8.53. C₁₂H₂₂O₄. Calculated %: C 54.97; H 8.39.

b) A mixture of 19.6 g (0.1 mole) of the di-(β -cyanethyl) ether of 1,3-butylene glycol, 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred at 95-97° for 6 hours (the mixture boiled). 20.6 g of the diethyl ester (XIV) was obtained:

b.p. 141-143° at 3 mm; n_D^{20} 1.4359; d_4^{20} 1.0292; MR_D 73.65; calculated 73.45 [3].

5.172 mg sub.: 10.995 mg CO₂; 4.095 mg H₂O. 6.651 mg sub.: 14.135 mg CO₂; 5.270 mg H₂O. Found %: C 58.02, 57.99; H 8.87, 8.87. C₁₄H₂₆O₄. Calculated %: C 57.93; H 8.97.

III. Reaction of Acrylonitrile With 1,4-Butylene Glycol

222 g (2.47 moles) of 1,4-butylene glycol, 22 g of a 40% aqueous solution of potassium hydroxide and 265 g (5 moles) of acrylonitrile were taken. 441 g of the di-(β -cyanethyl) ether of 1,4-butylene glycol (III) was obtained:

b.p. 183-191° at 3 mm; m.p. 38-39°; n_D^{20} 1.4516; d_4^{20} 1.0289; MR_D 51.39; calculated 51.30.

6.112 mg sub.: 13.741 mg CO₂; 4.473 mg H₂O. 5.896 mg sub.: 13.301 mg CO₂; 4.342 mg H₂O. Found %: C 61.35, 61.56; H 8.19, 8.24. C₁₀H₁₈O₂N₂. Calculated %: C 61.22; H 8.16.

Hydrogenation of the Di-(β -cyanethyl) Ether of 1,4-Butylene Glycol

199 g (1 mole) of the di(β -cyanethyl) ether of 1,4-butylene glycol, 600 ml of methyl alcohol, saturated with ammonia, and 12 g of Raney nickel were taken. The hydrogenation was carried out at 95-105° for 1 hour at an initial hydrogen pressure of 85 atm. The theoretical quantity of hydrogen (91 liters) was absorbed.

185 g of the di-(γ -aminopropyl) ether of 1,4-butylene glycol (XXIII) [7] was obtained:

b.p. 134-137° at 4 mm; n_D^{20} 1.4619; d_4^{20} 0.9624; MR_D 58.25; calculated 58.51.

12.310 mg sub.: 1.146 ml N₂ (22°, 757 mm). 4.821 mg sub.: 0.560 ml N₂ (22°, 757 mm). Found %: N 13.67, 13.39. C₁₀H₂₄O₂N₂. Calculated %: N 13.72.

Upon stirring equimolecular quantities of the diamine obtained and adipic acid in alcohol a crystalline salt with a m.p. of 114-115.5° was formed.

3.485 mg sub.: 0.1736 ml N₂ (18°, 730 mm). 3.270 mg sub.: 0.1588 ml N₂ (20°, 732 mm). Found %: N 5.58, 5.43. C₁₈H₃₄O₄N₂. Calculated %: N 5.64.

Hydrolysis of the Di-(β -cyanethyl) Ether of 1,4-Butylene Glycol

A mixture of 63 g (0.32 mole) of the di-(β -cyanethyl) ether of 1,4-butylene glycol and 130 ml of concentrated hydrochloric acid was stirred at 75-80° for 4 hours and at 100° for 15 minutes. 73.5 g of the dicarboxylic acid (VIII) with a m.p. of 90° (from benzene) was obtained.

6.350 mg sub.: 11.920 mg CO₂; 4.405 mg H₂O. 6.442 mg sub.: 12.070 mg CO₂; 4.370 mg H₂O. Found %: C 51.23, 51.13; H 7.76, 7.59. C₁₀H₁₈O₄. Calculated %: C 51.28; H 7.69.

Alcoholysis of the Di-(β -cyanethyl) Ether of 1,4-Butylene Glycol

a) A mixture of 19.6 g (0.1 mole) of the di-(β -cyanethyl) ether of 1,4-butylene glycol, 50 ml of methyl alcohol and 30 g of concentrated sulfuric acid was stirred at 82-85° (the mixture boiled) for 10 hours. 16.8 g of the dimethyl ester (XV) was obtained; it consisted of a colorless liquid with a characteristic odor:

b.p. 146-148° at 4 mm; n_D^{20} 1.4389; d_4^{20} 1.0691; MR_D 64.41; calculated 64.21.

5.317 mg sub.: 10.780 mg CO_2 ; 4.100 mg H_2O . 8.334 mg sub.: 16.794 mg CO_2 ; 6.340 mg H_2O . Found %: C 55.32, 55.00; H 8.63, 8.52. $C_{12}H_{22}O_5$. Calculated %: C 54.97; H 8.39.

b) A mixture of 120 g (0.6 mole) of the di-(β -cyanethyl) ether of 1,4-butylene glycol, 300 ml of ethyl alcohol and 150 g of concentrated sulfuric acid was stirred at 93-95° (the mixture boiled) for 6 hours. 117 g of the diethyl ester (XVI) was obtained:

b.p. 154-155° at 4 mm; n_D^{20} 1.4380; d_4^{20} 1.0329; MR_D 73.70; calculated MR_D 73.45.

4.582 mg sub.: 9.791 mg CO_2 ; 3.695 mg H_2O . 5.051 mg sub.: 10.752 mg CO_2 ; 4.075 mg H_2O . Found %: C 58.37, 58.08; H 9.02, 9.03. $C_{14}H_{26}O_6$. Calculated %: C 57.93; H 8.97.

IV. Reaction of Acrylonitrile With Diethylene Glycol

115 g (1.1 moles) of diethylene glycol, 10 g of a 40% aqueous solution of potassium hydroxide and 115 g (2.2 moles) of acrylonitrile were taken. 224.5 g of the di-(β -cyanethyl) ether of diethylene glycol (IV) was obtained:

b.p. 185-189° at 0.5 mm; n_D^{20} 1.4530 [8].

Hydrogenation of the Di-(β -cyanethyl) Ether of Diethylene Glycol

21.2 g (0.1 mole) of the di-(β -cyanethyl) ether of diethylene glycol, 55 ml of methyl alcohol saturated with dry ammonia, and 2 g of Raney nickel were taken. Hydrogenation was carried out at 100-110° for 1 hour 20 minutes at an initial hydrogen pressure of 80 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed. 18 g of the di-(γ -aminopropyl) ether of diethylene glycol (XXIII) was obtained:

b.p. 146-148° at 4 mm; n_D^{20} 1.4642; d_4^{20} 1.0107; MR_D 60.08; calculated 60.15.

8.640 mg sub.: 1.008 ml N_2 (21°, 745 mm). 9.905 mg sub.: 1.123 ml N_2 (20°, 750 mm). Found %: N 13.30, 13.04. $C_{10}H_{24}O_3N_2$. Calculated %: N 12.72.

The corresponding phenylcarbamide with a m.p. of 100-102° (from alcohol) was prepared by the action of phenylisocyanate.

2.970 mg sub.: 0.3254 ml N_2 (19°, 730 mm). 3.335 mg sub.: 0.3646 ml N_2 (20°, 733 mm). Found %: N 12.30, 12.30. $C_{11}H_{20}O_3N_2$. Calculated %: N 12.39.

Hydrolysis of the Di-(β -cyanethyl) Ether of Diethylene Glycol

A mixture of 29 g (0.135 mole) of the di-(β -cyanethyl) ether of diethylene glycol and 60 ml of concentrated hydrochloric acid was stirred at 70° for 4 hours and at 95° for 20 minutes. 30.8 g of the dicarboxylic acid (IX) was obtained in the form of a light yellow oil, which did not crystallize [2].

Alcoholysis of the Di-(β -cyanethyl) Ether of Diethylene Glycol

a) A mixture of 21.2 g (0.1 mole) of the di-(β -cyanethyl) ether of diethylene glycol, 50 ml of methyl alcohol and 25 g of concentrated sulfuric acid was stirred at 82-86° (the mixture boiled) for 10 hours. 20.1 g of the dimethyl ester (XVII) was obtained:

b.p. 155-157° at 3 mm; n_D^{20} 1.4429; d_4^{20} 1.1161; MR_D 66.11; calculated 65.85.

5.185 mg sub.: 9.830 mg CO_2 ; 3.690 mg H_2O . 4.968 mg sub.: 9.430 mg CO_2 ; 3.492 mg H_2O . Found %: C 51.86, 51.80; H 7.96, 7.87. $C_{12}H_{22}O_7$. Calculated %: C 52.17; H 7.97.

b) A mixture of 21.2 g (0.1 mole) of the di-(β -cyanethyl) ether of diethylene glycol, 60 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred at 96-98° (the mixture boiled) for 6 hours. 22.1 g of the diethyl ester (XVIII) was obtained:

b.p. 167-169° at 4 mm; n_D^{20} 1.4395; d_4^{20} 1.0726; MR_D 75.11; calculated 75.09.

9.30 mg sub.: 18.80 mg CO_2 ; 7.23 mg H_2O . 8.88 mg sub.: 17.88 mg CO_2 ; 6.89 mg H_2O . Found %: C 55.17, 54.97; H 8.69, 8.63. $C_{14}H_{26}O_7$. Calculated %: C 54.90; H 8.49.

V. Reaction of Acrylonitrile With Ethylene Cyanhydrin

915 g (12.9 moles) of ethylene cyanhydrin, 65 g of a 40% aqueous solution of potassium hydroxide and 684 g (12.9 moles) of acrylonitrile were taken. 1476 g of the di-(β -cyanethyl) ether (V) was obtained:

b.p. 167-174° at 5 mm; n_D^{20} 1.4418 [8].

Hydrogenation of the Di-(β -cyanethyl) Ether

12.5 g of the di-(β -cyanethyl) ether, 50 ml of methyl alcohol saturated with dry ammonia, and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 100-115° for 30 minutes at an initial hydrogen pressure of 140 atm. The theoretical quantity of hydrogen (9.0 liters) was absorbed. 10.2 g of the di-(γ -aminopropyl) ether (XXV) was obtained:

b.p. 72° at 4 mm; n_D^{20} 1.4595 [6].

Hydrolysis of the Di-(β -cyanethyl) Ether

1250 ml of concentrated hydrochloric acid was added to 400 g (3.2 moles) of the di-(β -cyanethyl) ether while it was being cooled with ice water and stirred. After the temperature of the mixture ceased to rise spontaneously, the stirring was continued for 4 hours at 70-80° and for 30 minutes at 95-98°. 507 g of the β,β' -di-(carboxyethyl) ether (X) was obtained:

m.p. 60.5-61.5° (from ether) [2].

Alcoholysis of the Di-(β -cyanethyl) Ether

a) A mixture of 250 g (2 moles) of the di-(β -cyanethyl) ether, 1000 ml of methyl alcohol and 500 g of concentrated sulfuric acid was stirred for 10 hours at 80-85° (the mixture boiled). 208.7 g of the di-(β -carboethoxyethyl) ester (XIX) was obtained:

b.p. 94-96° at 4 mm; n_D^{20} 1.4288; d_4^{20} 1.1127; MR_D 44.01; calculated 44.09.

4.925 mg sub.: 9.198 mg CO₂; 3.290 mg H₂O. 6.556 mg sub.: 12.163 mg CO₂; 4.437 mg H₂O. Found %: C 50.96, 50.63; H 7.47, 7.58. C₉H₁₄O₅. Calculated %: C 50.52; H 7.37.

b) A mixture of 62 g (0.5 mole) of the di-(β -cyanethyl) ether, 250 ml of ethyl alcohol and 150 g of concentrated sulfuric acid was stirred for 8 hours at 90-98° (the mixture boiled). 58 g of the di-(β -carboethoxyethyl) ester (XX) [9] was obtained:

b.p. 124-125° at 7 mm; 104-106° at 4 mm; n_D^{20} 1.4274; d_4^{20} 1.0522; MR_D 53.24; calculated 43.33.

12.26 mg sub.: 24.58 mg CO₂; 9.23 mg H₂O. 9.38 mg sub.: 18.87 mg CO₂; 6.89 mg H₂O. Found %: C 54.71, 54.85; H 8.42, 8.22. C₁₃H₁₈O₅. Calculated %: C 55.05; H 8.26.

VI. Polycondensation of the Salt of the Di-(γ -aminopropyl) Ether of 1,4-Butylene Glycol and Adipic Acid (Salt AB)

The polycondensation was carried out in a test tube supplied with a stopper with a tube for passing in nitrogen and one for eliminating the water formed. The nitrogen was freed from oxygen by passage through pyrogallol, dried with sulfuric acid and calcium chloride; after this the nitrogen was passed over copper heated to 470° and, finally, over phosphoric anhydride.

6 g of the salt was placed in the test tube and was heated to the melting point and after fusion, a constant stream of nitrogen was passed in. In the course of 5 hours, the temperature of the bath was raised from 160 to 270°. The heating was continued for 40 minutes at 270°. Water was evolved in the course of the first three hours. On cooling, the melt solidified into a light, creamy mass. It could be cut with a knife, clung to the glass, and was washed off with water.

A portion of the product obtained was heated in a vacuum at 220-240° for 2 hours. The product became brown colored and harder.

VII. Joint Polycondensation of Salt AB With the Salt of Adipic Acid and Hexamethylene Diamine (Salt AH)

In a ratio of 1:3. Taken: 11.25 g of salt AH and 3.75 g of salt AB. The mixture was heated for 1 hour to 250° and then for 4 hours at 250-260° in a vacuum. A light brown solid product with a coralline cross section was obtained.

In ratio of 1:1. a) Taken: 7.5 g of salt AH and 7.5 g of salt AB. The mixture was heated for 1 hour to 250° and then for 4 hours at 250-260° in a vacuum. A light cream elastic polymer which could be cut with a knife was obtained. /b) Taken: 3 g of salt AH and 3 g of salt AB. In the course of 3 hours, the temperature was raised

from 160 to 240° and then the mixture was heated for 1.5 hours at 240-250°. A white solid polymer with a cornulate cross section was obtained.

In a ratio of 3:1. Taken: 3.75 g of salt AH and 11.25 g of salt AB. The mixture was heated in a vacuum at 250-260° for 2 hours. A dark grey polymer which could be cut with a knife only with difficulty was obtained.

SUMMARY

The hydrogenation, hydrolysis and alcoholysis of β -cyanethyl ethers of ethylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, diethylene glycol and ethylene cyanhydrin were studied. The corresponding diamines, dicarboxylic acids and their esters, containing oxygen heteroatoms in the chain and able to be used for the preparation of new polyamides with increased hydrophilic properties, were prepared in high yields.

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INVESTIGATION OF THE NATURE OF THE CATALYSTS USED FOR ISOMERIZATION AND POLYMERIZATION OF HYDROCARBONS

I. CONCERNING THE CAUSE OF THE CATALYTIC ACTIVITY OF TITANIC ACID

G. A. Rudakov and Z. S. Khomenko

In connection with the catalytic isomerization and polymerization of hydrocarbons in the presence of clay, which was initiated by L. G. Gurvich [1], the chemical transformations of the separate compounds, the mechanism of the processes which proceed, and also the nature of the catalysts causing the indicated reactions have been studied in recent years.

On the basis of the results obtained during the study of the catalytic conversions of pinene on active clays and of the close congruence of these conversions with the conversions of pinene under the influence of certain acids, and also keeping in mind the work of V. I. Vernadsky [2] and of P. A. Zemyatchensky [3], which have made it possible to chemically characterize the clay as a mixture of aluminum silicic acids, V. E. Tishchenko and G. A. Rudakov [4] came to the conclusion that the catalytic properties of active clays are due to the acid nature of the aluminum silicates of which they are formed. This explanation of the activity of aluminum silicate catalysts, published as early as 1933, is shared by the majority of chemists at the present time.

If the acid nature of the clays and of synthetic aluminum silicates used along with the clays as catalysts is generally accepted at the present time, the question of the cause of the acid nature of the said aluminum silicates, which fundamentally differ in their properties from silicic anhydride and aluminum hydroxide, remains in dispute.

Certain investigators [5, 6] assume that the acid properties of aluminum silicate catalysts are due to the presence on them of surface sorbed mineral acids and basic salts of aluminum. These views are supported by certain properties of carefully dialyzed gels of aluminum silicates, including the absence of electrical conductivity and the weak catalytic activity, but are inconsistent with the possibility of obtaining active aluminum silicate catalysts by aqueous hydrolysis of mixtures of the ethyl ester of silicic anhydride and aluminum isopropylate [7].

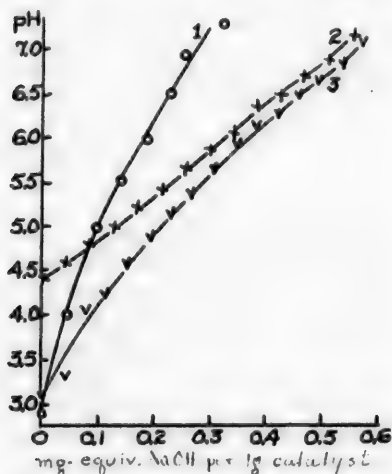


Fig. 1. Potentiometric titration curves of titanium catalysts with 0.1 N NaOH. 1) Catalyst ED-2; 2) catalyst 1-52; 3) catalyst 16-52.

Ross and Hendriks [8], Thomas [7] and other investigators explained the presence of acid properties in aluminum silicates by the peculiarities of their structure, which fundamentally differentiate them from the silica which enters into their composition. In agreement with the representation of these authors, the Si atom with a valence of 4 and a coordination number 4, which is substituted in the aluminum silicate lattice for an Al atom with a valence of 3 and a coordination number 4, leads to the phenomenon of a charge in the lattice which is compensated for by the hydrogen atoms which enter into it and subsequently are capable of ready exchange.

The views of Ross and Hendriks and also of Thomas on the cause of the acid properties of aluminum silicates encounter a number of objections. These objections have been made known by K. G. Mieserov [9] in his review which recently appeared.

He gives his explanation of the acid nature of aluminum silicates, which consists of the assumption that acidic aluminum silicates have an exchangeable Al ion which replaces the hydrogen in the SiOH groups and is capable of adding water with the formation of the complex $\left[\text{>AlOH} \right]^- \text{H}^+$, with a mobile hydrogen ion.

It seems that the points of view set forth on the cause of the activity of aluminum silicate catalysts are at fault in attempting to give a single explanation of the formation of the hydrogen ion which is capable of ready exchange in such complex substances as aluminum silicates. It should be noted also at the same time that the majority of investigators ignore other, analogously acting catalysts, which is incorrect, since the results of the study of catalysts which act similarly to aluminum silicate but have a simpler composition, may possibly turn out to be useful for the understanding of the causes of the activity of aluminum silicate catalysts.

Of the catalysts with simpler compositions than aluminum silicate catalysts, titanitic acid, to which the present work has been devoted, merits attention. Titanitic acid has been employed for the isomerization of pinene into camphene and monocyclic terpenes [10] and of Δ^3 -carene into Δ^4 -carene [11].

TABLE 1

Comparative Characteristics of Catalysts

Catalyst No.	Loss from roasting (in %)	Na ₂ O (in %)	pH	NaOH consumption		Surface (in m ² /g)	Activity with respect to pinene		
				To bring the pH of a suspension of 1 g of the catalyst in water to 7 (in mg equiv.)	To neutralize the CH ₃ COOH evolved as a result of the exchange reaction of 1 g of catalyst with CH ₃ COONa (in mg equiv.)		Temperature (in °)	% of catalyst	Duration (in hours)

Titanium catalyst obtained by the decomposition of sodium titanate with dilute acid

2-51	8.7	4.38	6.1	0.105	—	—	135	1	8
1-52	7.9	2.62	4.54	0.530	0.565	180	135	1	1
							160	0.2	0.75
16-52	9.5	0.23	3.06	0.560	0.655	132	160	0.2	0.75

Titanium catalyst obtained by electrodialysis of sodium titanate

ED-2	—	0.49	2.9	0.300	—	114	135	2	2
Activated Chasov-Yar clay									
8-52	—	—	2.67	0.183	—	80	125	1	3
							160	0.25	1-15

The titanitic acid used as a catalyst is ordinarily obtained by the hydration of titanium dioxide by aqueous solutions of NaOH, with subsequent decomposition of the titanate formed with dilute acids. The catalyst, carefully washed free from the acid taken for decomposing the titanate and dried, has pronounced acid properties. The pH value of aqueous suspensions of the catalyst lies between 3 and 6, depending on the extent of the decomposition of the titanate. The catalyst, similarly to aluminum silicate, has a mobile, readily exchangeable hydrogen ion, which can be determined via direct potentiometric titration of an aqueous suspension of the catalyst by NaOH solution (Fig. 1) or via titration with CH₃COOH evolved as a result of an exchange reaction of the catalyst with 1 N CH₃COONa solution [12].

The acid properties of titanium catalyst are not due to sorbed acid in it, since catalyst with the very same properties was obtained by the electrodialysis of sodium titanate, i.e., without the use of acid. Comparison of the activity of various samples of catalyst was carried out according to the rate of the isomerization of pinene. This reaction is very convenient for the indicated object, since it proceeds at comparatively low temperatures (130-160°), due to which it is not complicated by thermal processes. It was established that the isomerization of pinene with titanitic acid proceeds even faster than with an equal quantity by weight of activated Chasov-Yar clay which has been repeatedly used as a catalyst for the indicated reaction [4, 13]. The greater activity of titanium catalyst than that of activated Chasov-Yar clay, appears to be a consequence of the higher content of hydrogen ions in the titanium catalyst which are capable of exchange, and of its greater specific surface. The results of the investigation of titanium catalysts and the results of their comparison with activated Chasov-Yar clay are set forth in Table 1.

The presence of strongly expressed acid properties and considerable catalytic activity approximates the behavior of titanitic acid to that of aluminum silicate catalysts, but not to its closest analogs — silicic acid and aluminum

hydroxide, which have very weakly expressed acid properties and little catalytic activity [7]. It is sufficient to state that for the complete isomerization of pinene at 155-160° in a period of 2 hours it is necessary to introduce 2% of silica gel as catalyst, i.e., 30 times more than of titanium catalyst or of activated Chasov-Yar clay.

The cause of so pronounced acid properties of titanitic acid can be explained by using the rule of electrostatic valency. In all forms of titanium dioxide, tetravalent titanium has a coordination number of 6, in accordance with which the strength of the titanium-oxygen bond in the lattice is equal to $\frac{2}{3}$. Since the coordination number of oxygen in lattices of titanium dioxide is equal to 3, the lattice has a neutral charge. In the case of hydration of the separate oxygen-titanium bonds, hydroxyl groups are formed. Since the strength of the oxygen-hydrogen bond is equal to 1, while the strength of the bond of the oxygen of the hydroxyl group with a titanium ion is equal to $\frac{2}{3}$, $\frac{1}{3}$ of the valence of oxygen remains unsaturated. As a result, in the titanium dioxide lattice hydrated from the surface, a negative charge appears which must be compensated for by hydrogen ions which enter into the lattice (one per each three hydroxyl groups). The cation which enters into the lattice must proceed from the same hydrating reagent, since during the hydration of titanium dioxide the $\text{Ti}-\text{O}-\text{Ti}$ groups which are hydrated require



the addition of one cation and two hydroxyl groups; as a result the second cation of the hydrating reagent enters into the lattice to neutralize its charge.

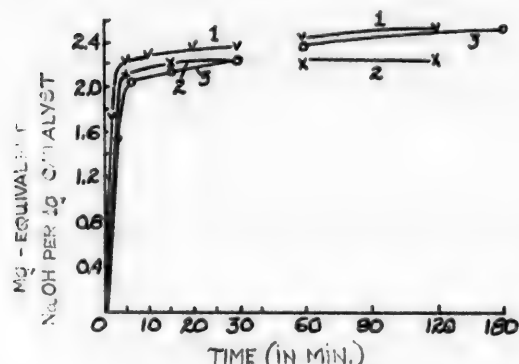


Fig. 2. Rate of absorption of NaOH from aqueous solutions by titanium catalyst. 1) Catalyst 1-52 + 0.1 N NaOH; 2) catalyst 1-52 + 0.01 N NaOH; 3) catalyst 16-52 + 0.01 N NaOH.

The considerations set forth are confirmed by the results obtained during the action of dilute NaOH solutions on titanium catalyst. During the addition to titanium catalyst of excess dilute NaOH solution a very rapid reaction proceeds, as a result of which 4 times more NaOH enters into the reaction than during the potentiometric titration to pH 7 of an aqueous suspension of the catalyst. Since an almost instantaneous hydration of the titanium-oxygen bond with an 0.01 N NaOH solution appears hardly probable, the different consumption of NaOH in the reaction with the catalyst in neutral and alkaline media must be explained otherwise. At pH values less than or equal to 7, an exchange of hydrogen ions for sodium ions proceeds, which neutralizes the lattice charge of the catalyst, which is also confirmed by the data obtained by the action on the catalyst of CH_3COONa solutions; in an alkaline medium there takes place, moreover, a reaction with the hydroxyl groups of the catalyst. The relation between the consumption of NaOH in both cases is in

excellent agreement with the requirement of the presence of one hydrogen ion for three hydroxyl groups joined to the Ti ion in the lattice (Table 2 and Fig. 2).

TABLE 2

Action of NaOH and CH_3COONa on Titanium Catalyst

Catalyst No.	Substances which react with 1 g of catalyst (in mg-equiv.)				A:D	B:D
	(A) NaOH during the raising of the pH of the suspension to 7	(B) CH ₃ COONa	NaOH in alkaline medium			
			(C) Total	(D) After raising the pH of the suspension to 7		
1-52	0.53	0.565	2.28	1.75	1:3.3	1:3.1
16-52	0.56	0.655	2.56	2.00	1:3.7	1:3

The data set forth circumstantially confirm the views of Thomas and other investigators concerning the cause of the catalytic activity of aluminum silicate catalysts. However, it is entirely probable that the activity of aluminum silicate catalysts can be evoked not only by the causes set forth, but also by others.

EXPERIMENTAL

1. Preparation of Sodium Titanate

The sodium titanate which served as the starting material for the preparation of the catalyst, was prepared in accordance with the data in the literature [10]: titanium dioxide was treated with a strong solution of sodium hydroxide while being heated under pressure, and the reaction product was washed with water until the NaOH was eliminated from it.

Metatitanic acid obtained by aqueous hydrolysis of $Ti(SO_4)_2$ containing 6-7% sulfuric acid, probably bound on account of incomplete hydrolysis, was also used as a starting material. The treatment of the metatitanic acid with NaOH solution was carried out at atmospheric pressure and led to complete splitting off of H_2SO_4 .

The sodium titanate obtained in both cases was identical. When dried at 105° , it consisted of a white powder and contained about 12% Na calculated on Na_2O . The loss from roasting amounted to around 8%; the pH of an aqueous suspension was 7-7.2. The quantity of sodium in the preparation showed that it consisted not of the sodium salt of titanic acid, but only of titanium dioxide hydrated from the surface.

2. Decomposition of the Sodium Titanate by Acids

The decomposition of the sodium titanate was also carried out in accordance with literature data [10], with weak aqueous solutions of acids (from 0.1 to 1%). Both mineral acids (HCl)₂ and organic acids ($HCOOH$, CH_3COOH) were used. If there was any problem of complete elimination of the sodium, the treatment was repeated a number of times. After decomposition with acid, the precipitate was carefully washed until complete elimination of the excess acid introduced, and was filtered on a Büchner funnel. The drying of the catalyst was carried out at 105° in a desiccator or under a vacuum at 100° .

3. Electrodialysis of the Sodium Titanate

The electrodialysis of the sodium titanate, shaken up in distilled water, was carried out between two parchment membranes at a potential difference of the platinum electrodes of up to 600 V. The operation was continued for around two months.

4. Activated Chasov Yar Clays

Chasov-Yar clay No. 5 was used for the experiments. The activation was carried out by treatment with hydrochloric acid under the usual conditions [4].

5. Determination of pH and Potentiometric Titration of the Catalysts

The determination of pH and the potentiometric titration were carried out with quinhydrone electrodes. 2.5 g samples of the catalysts were used; before the titration they were shaken up in 12.5 ml of water. During the titration, after the addition of each portion of NaOH solution, we waited for about 10 minutes in order that the reaction might be concluded, although equilibrium was rapidly established. Thus, for example, the pH of a suspension of titanium catalyst, neutralized with NaOH to a pH of 6.97, was 6.76 after 24 hours.

6. Determination of Sodium in the Titanium Catalyst

A portion of the catalyst, equal to 0.2-0.3 g was treated 5 times in succession with 15 ml of a 4% boiling solution of HCl. The duration of each treatment amounted to 2-3 minutes. After five treatments the precipitate was washed on a filter with a 4% solution of HCl. The partially dissolved titanium salt was precipitated from the filtrate with ammonia and the filtrate concentrated, after which the sodium was precipitated in the form of sodium zinc uranyl acetate, or after elimination of the ammonium salts was determined in the form of NaCl.

7. Determination of the Specific Surfaces of the Catalysts

The determination of the specific surfaces of the catalysts was made on the basis of the amount of methylene blue adsorbed by the catalysts. A sample of about 0.1 g of the catalyst was added to 60 ml of a 0.15% solution of the dye and shaken on a machine for 2 hours. After about 12 hours, the catalyst was precipitated on the centrifuge while the solution was analyzed colorimetrically after 100 fold dilution. The calculation of the surface was based on the fact that 1 mg of methylene blue is adsorbed by 1 square meter of catalyst surface [14].

8. Action of Excess NaOH on the Titanium Catalyst

200 ml of an 0.01 or 0.1 N NaOH solution was added to a 0.5 or 5 g sample of the catalyst placed in a 200 ml measuring flask. The flask was shaken periodically and samples were taken from it with a pipet, which were titrated after rapid filtration.

SUMMARY

1. As a catalyst of the isomerization of pinene, titanitic acid has no less activity than aluminum silicate catalyst.
2. The activity of titanium catalyst is due to the presence in it of hydrogen ions which are capable of ready exchange, or in other words, to its acid properties.
3. The preparation of active titanitic acid via electrodialysis of its sodium salt demonstrates that the activity of titanium catalyst is due to the properties of titanitic acid, and not to the presence of adsorbed acids or basic salts.
4. The high catalytic activity and pronounced acidity approximates titanitic acid in its properties to aluminum silicates, but not to its closest analogs — silicic acid and aluminum hydroxide. An explanation of this was given, based on the specific peculiarities of the lattice structure of titanium dioxide, which results in the necessity of one hydrogen entering into its composition for each three hydroxyl groups which are formed during its surface hydration.
5. The study of the action of NaOH solutions on titanium catalyst confirmed the development of the representation of the cause of the catalytic activity of titanitic acid.

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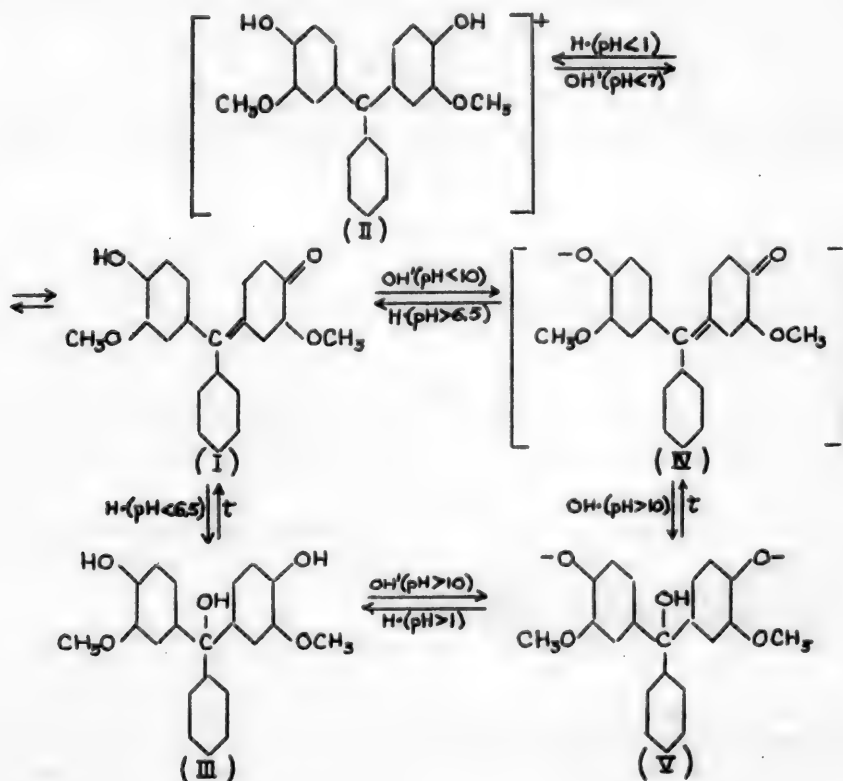
INVESTIGATION IN THE FIELD OF HYDROXYFUCHSONE

XIX [1]. INFLUENCE OF THE NITRO GROUP AND HALOGENS ON THE INDICATOR PROPERTIES OF DERIVATIVES OF 3,3'-DIMETHOXYBENZAURIN

I. S. Ioffe and B. G. Belenky

In one of the preceding communications [2], the indicator properties of certain hydroxyfuchsones of the aurin and benzaurin groups were considered by one of us. The most interesting as regards indicator properties was 3,3'-dimethoxybenzaurin (I). In the non-ionized state, it forms yellow solutions. In a mineral acid medium, it is dissolved with an intense violet coloration, the carrier of which appears to be the onium cation (II). The stability of the latter depends on the hydrogen ion concentration. In the presence of reduced acidity of the medium, the intensity of the coloration gradually falls and at a pH greater than 1 the solution is decolorized. We initially assumed that this was associated with cleavage of a proton and with regeneration of the initial dye. However, newer observations described below, show that the decolorization of the solution is due primarily to hydration of the dye and formation of the carbinol compound (III).

In a weakly alkaline medium 3,3'-dimethoxybenzaurin is dissolved with a bright blue color, the carrier of which appears to be the anion of the dye (IV). Upon increasing the hydroxyl ion concentration, the solution gradually is decolorized as a result of the addition of hydroxyl groups and formation of the still colorless anion of the carbinol compound (V). On heating, the decolorized solution again exhibits the blue color of the dye anion (IV). Upon acidification of the colorless solution with acetic acid, the carbinol compound (V) precipitates. Upon acidification



of the alkaline solutions with hydrochloric acid, and equally during the treatment of the carbinol compound (III) with hydrochloric acid, the onium cation (II) is formed. All the conversions described are incorporated in the scheme (see above).

In the development of this investigation, we studied the indicator properties of the 3,3'-dimethoxybenzaurin derivatives containing nitro groups and halogens in various positions of the benzene nucleus, which were described in the preceding communications [1, 3].

To study the influence of nitro groups and halogens on the conditions of formation of the onium cations of type (II) and on their stability to hydrolysis, we added approximately 0.5 ml of 0.00025 N alcoholic solution of the base of each dye to 9.5 ml of hydrochloric acid, subsequently lowering the concentration from 10 to 0.1 N. The intensity of the violet coloration which appeared, which characterizes the quantity of onium cation which was formed, we colorimetrically compared with the intensity of the coloration of a standard solution of a sample of the same weight of the corresponding dye in 10 N hydrochloric acid, in which the dye is entirely converted into the onium cation. The results obtained are set forth in Table 1.

TABLE 1

Dye	Normality of HCl							
	10	5	3	2	1	0.5	0.2	0.1
3,3'-Dimethoxybenzaurin	100	100	92	74	33	12.5	2	0
2''-Br- } 3,3'-Dimethoxybenzaurin	100	96	73	49	19	7	0	0
2''-Cl- }	100	96	68	43	17	6	0	0
3''-Br- }	100	95	58.5	24.5	5	0	0	0
3''-Cl- }	100	96	59.5	25.5	5	1	0	0
4''-Br- }	100	100	82	54	16	4	0	0
4''-Cl- }	100	100	84	56	18	5	0	0
3''-NO ₂ - }	100	79.5	22	6	0	0	0	0
4''-NO ₂ - }	100	76.5	17.5	5	0	0	0	0

These results are graphically portrayed in Figs. 1, 2, and 3, on which the pH values calculated from the hydrochloric acid concentration according to the data of Harned and Owen [4] are plotted on the abscissa, while the percent content of the onium cation in the equilibrium mixture is plotted on the ordinate.

For a more graphic comparison of the results obtained, we have determined for each of the dyes studied the pH value at which the equilibrium state is characterized by the presence of 50% of the onium cation. These data are set forth in Table 2.

TABLE 2

Substituent	H	p-Cl	p-Br	o-Br	o-Cl	m-Cl	m-Br	m-NO ₂	p-NO ₂
pH	-0.06	-0.24	-0.27	-0.31	-0.48	-0.525	-0.535	-0.86	-0.905

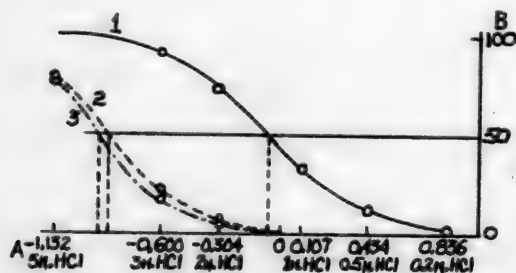


Fig. 1. A) pH (normality of HCl); B) percent content of onium cation in the equilibrium mixture. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO₂; 3) p-NO₂.

The data of Tables 1 and 2 and the figures show that with the presence in the benzene nucleus of halogens or nitro groups, the capacity of the corresponding 3,3'-dimethoxybenzaurin derivatives for addition of a proton with formation of the onium cation, i.e., the basicity of the dye, is lowered. To form the onium cations of these dyes a higher hydrochloric acid concentration is necessary; the stability to hydrolysis of the cations which are formed falls.

A particularly strong influence is exerted by the presence of nitro groups. 3''-Nitro- and 4''-nitro-3,3'-dimethoxybenzaurins do not even form onium cations in 1 N hydrochloric acid. The influence of halogens is exerted to a lesser degree, and the chloro- and bromo- derivatives yield approximately identical results. In the case of halogen

derivatives the position of the halogen is important. The greatest lowering of the basicity of the dye is caused by the presence of halogen in the m-position to the central carbon atom.

TABLE 3

pH	Substituent								
	H	o-Br	o-Cl	m-Br	m-Cl	p-Br	p-Cl	m-NO ₂	p-NO ₂
7.79	35	46	45	41	40.5	40	40	49	54.5
7.93	43	54	53	49.5	48.5	47.5	48	57.5	62.5
8.09	52	63.5	62.5	58	57.5	56.5	57	66	70.5

During the study of the influence of the nitro group and halogens on the indicator properties of 3,3'-dimethoxybenzaurin derivatives in the weakly alkaline zone, we used as standard a solution of the dye in a borate buffer with a pH equal to 9.5. In such a solution, the dye is almost wholly dissociated with the formation of the color specified for

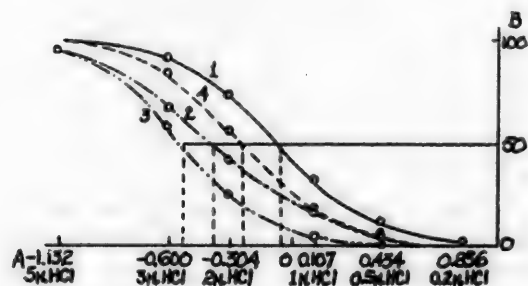


Fig. 2. A) pH (normality of HCl); B) percent content of onium cation in the equilibrium mixture. 1) 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl

It is evident from the figure that the points found for all the dyes are distributed on parallel straight lines with inclinations, the tangent of the angle of which is equal to 1. This shows that the dependence of the ionization of all the dyes studied on the pH of the medium is determined by the equation

$$pK = pH - \log \frac{[A]}{[AN]}$$

Therefore, using Fig. 4, one can graphically determine the pK value, since it corresponds for each dye to the point of intersection of the straight line corresponding to the given dye with the abscissa. The pK values found are set forth in Table 4.

TABLE 4

Substituent	H	o-Br	o-Cl	m-Br	m-Cl	p-Br	p-Cl	m-NO ₂	p-NO ₂
pK	8.06	7.86	7.88	7.96	7.95	7.97	7.98	7.80	7.71

benzaurin derivatives to dissociate in weakly alkaline medium with the formation of the colored anion of the dye; this influences the lowering of the values of pK. However, such a lowering is comparatively small. It amounts to 0.3 for the nitro compounds, and the lowering varies within the range 0.2-0.1 for the halogen derivatives, depending on the position of the halogen.

The complex of reactions which characterize the indicator properties of the hydroxyfuchsones includes the conversion of the dye into the corresponding carbinol derivatives. Such conversions have up to now, only been observed in alkaline medium; under these conditions, the coloring of the dye anion, which adds a hydroxyl ion, is converted into the colorless anion of carbinol compounds of type (V). Such conversions proceed appreciably for 3,3'-dimethoxybenzaurin at a pH of around 11. We studied the influence of nitro groups and halogens on the corresponding conversions of 3,3'-dimethoxybenzaurin.

In test tubes containing 9.5 ml of a solution of various concentrations with precisely measured pH, we introduced about 0.5 mg of an 0.0005 M alcoholic solution of the dye, after which the carefully shaken mixture was left in a dark place for 24 hours. After this interval of time, equilibrium was established between the colored anion of the dye and the colorless anion of the carbinol compound.

the anion type (IV), the solutions obtained were stable during storage and did not change the intensity of the color. With such a standard solution each dye was compared as regards intensity of color of the solution with the same dye with a pH in the range 7.8-8.1, and the optical density was measured for this with the aid of an SF-11 spectrophotometer. We calculated the degree of acid dissociation of the dye under study by the pH differences according to the results obtained. The results obtained are set forth in Table 3.

These data are graphically illustrated in Fig. 4, where the pH values are plotted on the abscissa and the values of the logarithm of the ratio of the concentration of the dye [A] to the concentration of non-dissociated dye [AN] are plotted on the ordinate.

The data of Tables 3 and 4 and of Fig. 4 show that the presence of halogen in the benzene nucleus and particularly of the nitro group, strengthens the capacity of the 3,3'-dimethoxy-

In control experiments, we became convinced as a result of colorimetric observations, that under the conditions of the experiment no destruction of the dye proceeded. 1 ml of the experimental solution was acidified with hydrochloric acid. Both an anion of the dye and an anion of the carbinol base thereupon were converted into the onium cation. Colorimetric determination of the latter showed that the quantity of both anions agreed in sum with the initial quantity of the dye.

TABLE 5

Dye	pH					
	10.67	10.80	10.95	11.11	11.26	11.43
3,3'-Dimethoxybenzaurin	88	68	53	40	30	23
3''-NO ₂ -	20	12	5	2	0	0
4''-NO ₂ -	16	8	3	1	0	0
3''-Cl-	51.5	37	24	15	10	6
3''-Br-	55	39	27	16	12	8
4''-Cl-	82.5	60	43	32	24	18
4''-Br-	85.5	62	45	34	24	18

The solutions obtained were compared according to the intensity of color with the standard solution obtained by dissolving a sample of the same weight of the dye in a borate buffer with a pH of 9.5. The results, which show the percent content of colored anion of the dye at various pH, are set forth in Table 5.

TABLE 6

Dye	pH					
	11.10	11.52	11.95	12.46	12.79	13.03
2''-Br-3,3'-dimethoxybenzaurin	100	96	81	55	33	17
2''-Cl-3,3'-dimethoxybenzaurin	100	88	67	32	16	7.5

The intensity of the color under the pH values indicated above does not change for o-halogen derivatives. The colored anions of these dyes are converted into anions of the carbinol compounds only in the presence of caustic alkalis at higher pH values, as is shown in Table 6.

TABLE 7

Substituent	H	o-Cl	o-Br	m-Cl	m-Br	p-Cl	p-Br	m-NO ₂	p-NO ₂
pH	10.98	12.21	12.54	10.68	10.71	10.88	10.90	~10.4	~10.3

The results obtained are portrayed graphically in Figs. 5 and 6, in which pH is plotted on the abscissa, while the percent content of the colored anion of the dye at the given pH is plotted on the ordinate.

For greater clarity, the pH values at which the content of the anion of the dye is equal to 50% are set forth in Table 7.

These data show that the content of colored anion is lowered in proportion to the increase of the concentration of hydroxyl ions, and that the given process is substantially influenced by the character and position of the substituent.

The nitro derivatives of 3,3'-dimethoxybenzaurin are distinguished by the least stability. The p-halogen derivatives are close to unsubstituted 3,3'-dimethoxybenzaurin; the m-halogen derivatives are somewhat less stable. The o-halogen derivatives, on the contrary, are

distinguished by a very high stability. This, evidently, is associated with the fact that the halogen anion found in the o-position to the central carbon atom, to a certain extent shields it and thereby hinders the addition to it of hydroxyl ions and the conversion of the dye anions into the anion of the carbinol compound. To overcome this hindrance, a

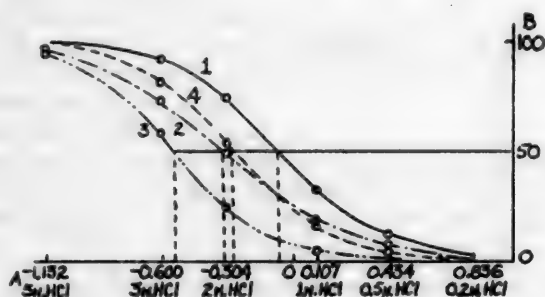


Fig. 3. A) pH (normality of HCl); B) percent content of the onium cation in the equilibrium mixture. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

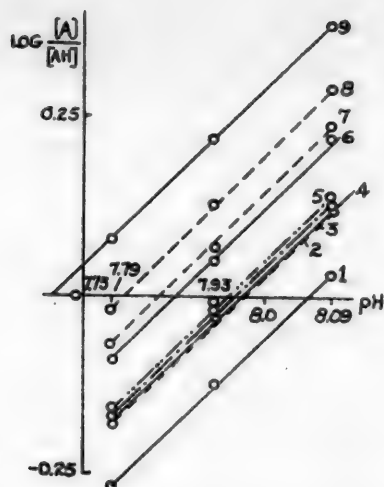


Fig. 4. Dependence of the ionization of the pigments on the pH of the medium. 1) 3,3'-Dimethoxybenzaurin; 2) m-Cl; 3) p-Cl; 4) p-Br; 5) m-Br; 6) o-Cl; 7) o-Br; 8) m-NO₂; 9) p-NO₂.

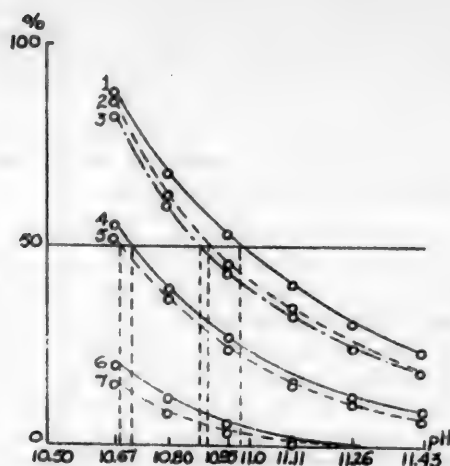


Fig. 5. Dependence of the content of colored anion of the dye on the pH. 1) 3,3'-Dimethoxybenzaurin; 2) p-Br; 3) p-Cl; 4) o-Br; 5) m-Cl; 6) m-NO₂; 7) p-NO₂.

higher hydroxyl ion concentration is necessary, and the shielding effect of bromine, with a larger atomic radius, exceeds the shielding effect of chlorine.

It turns out that the hydroxyfuchsones are capable of being converted into the corresponding carbinol compounds not only in alkaline medium, but also in weakly acidic medium. The shielding action of halogens in the o-position to the central carbon atom also takes place under these conditions.

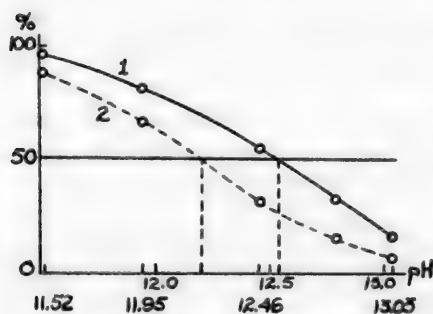


Fig. 6. Dependence of the content of colored anion on the pH. 1) o-Br; 2) o-Cl.

This previously unnoted property of hydroxyfuchsones was detected by us for the first time during the dilution of hydrochloric acid solutions of 3,3'-dimethoxybenzaurin and its derivatives, and also during the addition of an alcoholic solution of the dye to dilute acids. We established that under these conditions, all the dyes studied by us, with the exception of the o-halogen derivatives, form, depending on the pH, almost colorless or weakly colored solutions. The o-halogen derivatives during analogous treatment yield bright yellow solutions. In all cases, however, during the addition of strong hydrochloric acid, the violet color which is characteristic of the onium cation is still produced. The measurement of the intensity of this coloration showed that the dye is not destroyed during such conversions, and that it forms an equilibrium mixture of various forms, the total of which is equal to the quantity of the initial dye.

TABLE 8

Dye	pH			
	5.89	6.11	6.34	6.50
3,3'-Dimethoxybenzaurin	2	4	6	8
m-Br-	4	7	11.5	19.5
m-Cl-	4.5	7.5	11.5	20
p-Br-	3.5	6	9	14.5
p-Cl-	3.5	6	9.5	15
m-NO ₂ -	6	11.5	17	22
m-NO ₂ -	13.5	23.5	31.5	37.5

We assumed on this basis that during the dilution of hydrochloric acid solutions of the hydroxyfuchsones there proceeds not only dissociation of the onium cation with cleavage of a proton, but also formation of the colorless carbinol compound (III), and that the relative rate of these processes depends on the structure of the dye. Preliminary experiments showed that for all the dyes, except the o-halogen dyes, a pale yellow color appeared at pH values in the range 5.5-6.5. On lowering the pH to 1, the solution again became colorless. Upon increase of the pH above 7, acid

dissociation began with the formation of the colored anion.

Therefore, we studied this process in the pH zone between 5.8 and 6.5. About 1 ml of 0.0005 M alcoholic solution of each dye was introduced into a test tube with 9 ml of buffer solution, and the intensity of the yellow color was measured colorimetrically, taking a solution of the same weight of dye in 10 ml of alcohol as the standard. The results obtained are set forth in Table 8.

The measurement of the intensity of the coloration of the o-halogen derivatives showed that at the experimental pH values, the dyes were not hydrated at all, which can only be explained by a shielding effect of the halogens in the o-position to the central carbon atom.

The data of Table 8 show that, in contrast to the conversions in alkaline medium, in a weakly acidic medium the content of the carbinol derivative is lowered proportionately as the hydrogen ion concentration decreases and the hydroxyl ion concentration increases. On the other hand, it is evident from the data of Table 8 that, in contrast with the conversions in alkaline medium, the presence of the nitro group hinders the formation of the carbinol compound, and increases the stability of the quinoid form of the dye. Halogens in the m- and p-positions also increases, although to a lesser degree, the stability of the colored quinoid form of the dye. Consequently, the mechanisms of formation of the carbinol compounds in strongly alkaline and weakly acidic media are different. In alkaline medium, the colored dye anion of type (IV) is attacked by the hydroxyl ion and adds the latter to the partially saturated central carbon atom, with the formation of one more negative charge on the quinoid oxygen atom, and with the formation of a colorless anion of the carbinol compound type (V). This process according to the mass action law, is accelerated during increased concentration of hydroxyl ions, to which the data of Table 5 and particularly of Fig. 5, convincingly attest. At diminished hydroxyl ion concentration, particularly with heating, the colorless anion of type (V) splits off hydroxyl and is converted back into the colored anion of type (IV).

In a weakly acidic medium it is increase not of hydroxyl ions but of hydrogen ions which facilitates the formation of the carbinol compounds even in the non-ionized state. When the pH is lowered below the isoelectric point, the coloration characteristic of the hydroxyfuchson dye gradually disappears, the solution becomes colorless and only in the presence of a considerable increase in the acidity of the medium, when the onium cation of the dye acquires stability, does the innate color of the latter arise.

The intensity of the color characteristic of the hydroxyfuchson dye fails to change in the pH range 5-6.5 only with the o-halogen derivatives under the influence of the shielding effect of the halogen atoms.

Conditions which counteract the shielding effect of halogens in the o-position to the central carbon atom are necessary to convert these dyes into the colorless carbinol compounds. On the basis of considerations set forth above, we assumed that a greater concentration of hydrogen ions was necessary for this, but one not below pH 1, at which the formation of onium cations is still possible. Our assumptions were confirmed by experiment.

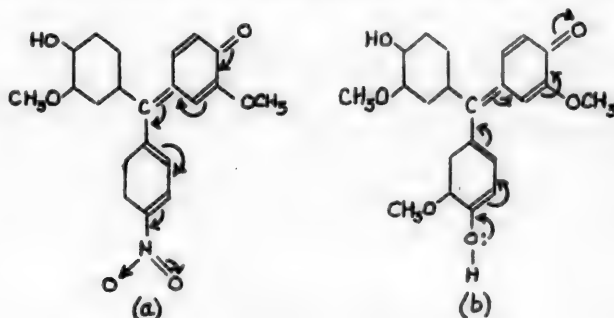
The intensity of the yellow color of solutions of o-halogen derivatives of 3,3'-dimethoxybenzaurin in solutions with a pH in the range 1-2 was compared colorimetrically with a standard solution at pH 6. It turned out to be equal on the average to 66% for the o-chloro derivative, while it was 82% for the o-bromo derivative.

It follows from these data that, actually, when the hydrogen ion concentration is increased, the shielding effect of halogens in the o-position is overcome -- to a greater extent for chlorine and to a lesser extent for bromine. These data, on the other hand, confirm that an increased concentration of hydrogen ions facilitates the conversion of hydroxyfuchson compounds into carbinol derivatives in the weakly acid zone.

Therefore, if the formation of the carbinol compound in alkaline medium depends on the attack of hydroxyl ions, then the formation of carbinol compounds in a weakly acidic medium reduces to the hydration of molecules of the hydroxyfuchson dye at the quinoid grouping, and the hydrogen ion concentration plays a decisive role therein.

The investigation carried out by us showed that the introduction into the benzene nucleus of 3,3'-dimethoxybenzaurin of a nitro group or of halogens influences all the indicator conversions of the dye. Under the influence of these substituents in the weakly acidic zone, the basic properties of the dye and its capacity to form onium cations are weakened and the stability of these cations is lowered. The capacity of the dye to dissociate with formation of colored anions, with corresponding lowering of the pK of dissociation is strengthened in the weakly alkaline zone under the influence of halogens and of the nitro group. In addition, these substituents influence the conversion of the dye into the corresponding carbinol compounds. In an alkaline medium, the presence of halogens and of the nitro group facilitates the formation of carbinol compounds at lower pH values. In a weakly acidic medium, these substituents, on the contrary, strengthen the stability of the dye and hinder their hydration.

Of the group of typical electron-acceptor substituents, the nitro group exerts the maximum influence, particularly when it is present in the p-position of the benzene nucleus. In drawing off electrons (scheme a), this group weakens the capacity of the dye to add a proton with the formation of an onium cation, i.e., weakens the basic properties of the dye. For the same reason, the nitro group causes the displacement of the density of the electron cloud of the bond between atoms of hydrogen and oxygen in the hydroxyl group toward the oxygen, thereby facilitating the dissociation of the dye in weakly alkaline medium with formation of the colored anion of the dye. The presence of the nitro group in the latter, by drawing off electrons, causes intensification of the positive charge on the central carbon atom, which facilitates the addition to it of a hydroxyl group at increased pH of the medium, with conversion into the anion of the carbinol derivative. During hydration in acid medium, when the hydrogen ions play a decisive role, the presence of the nitro group weakens the basicity of the dye and hampers its hydration.



In the light of these considerations, the difference between the aurin dye group from the benzaurin dye, which was noted previously [2], is understandable. In dyes of the aurin group, for example in rubrocol (b), the presence of an electron donor group in the p-position exerts an influence opposed to the influence of the electron acceptor nitro group. Rubrocol, therefore, possesses more highly basic properties, and forms onium cations which are stable at higher pH values. The rubrocol anions formed in alkaline medium also possess a greater stability and are converted into anions of the carbinol compounds only in the presence of concentrated alkali.

In the halogen derivatives of 3,3'-dimethoxybenzaurin which were studied by us, if one excludes the steric hindrances during the hydration of o-halogen derivatives, the influence of halogens, which have lesser electron acceptor properties than the nitro group, and are arranged at a distance from the hydroxy and oxo- groups in the benzene nucleus, is manifested in the same direction as that of the nitro group, but to a lesser extent.

SUMMARY

The influence of nitro groups and halogens in the benzene nucleus of 3,3'-dimethoxybenzaurin on the indicator properties of the dye was studied.

It was shown that the presence of these substituents weakens the basic properties of the dye, its capacity to form onium cations in a strongly acidic medium, and lowers the stability of the onium cations. In a weakly alkaline medium, the presence of these substituents strengthens the capacity of the dye to dissociate with the formation of anions of the dye and lowers their pK of dissociation. At increased pK values of the medium, these substituents facilitate the conversion of colored anions of the dye into the colorless anions of the carbinol compounds. Only in the o-halogen derivatives does the presence of halogens in the o-position to the central carbon atom, which shields the latter from the attack of hydroxyl groups, hamper the formation of anions of the carbinol derivatives. It was established that derivatives of 3,3'-dimethoxybenzaurin are also converted into the carbinol compounds in a weakly acidic medium; this process, in contradistinction to the formation of carbinol compounds in alkaline medium, is promoted by increased concentration not of hydroxyl ions, but of hydrogen ions. Therefore, in the presence of dilute solutions of the onium salts of the dye not only cleavage of a proton with formation of the hydroxyfuchson dye occurs, but also hydration of the latter with decolorization of the solution. Only in the pH range between 5.5 and 6.5 in an equilibrium mixture is there an insignificant quantity of the non-hydrated dye present. The presence of halogens in the o-position to the central carbon atom, which shields the latter, also gives rise to steric hindrance during this hydration of the dye.

Of all the substituents considered above, the electron acceptor nitro group exerts a maximum influence in all the conversions at the above indicated concentrations. Electron donor groups exert influence in the opposite direction.

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• See Consultants Bureau Translation, page 2051.

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INVESTIGATION IN THE FIELD OF HYDROXYFUCHSONE DYES

XX. INFLUENCE OF THE NITRO GROUP AND HALOGENS ON THE COLOR OF DERIVATIVES OF 3,3'-DIMETHOXYBENZAURIN

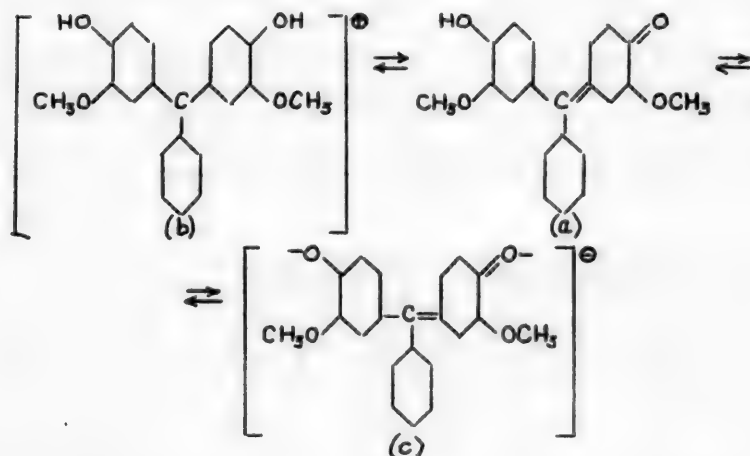
I. S. Ioffe and B. G. Belenky

The influence of the character and position of the substituents on the color of the dye has been studied in very great detail in the series of basic triphenylmethane dyes. It has been established that a considerable deepening of the color occurs in proportion to increase in the basicity of the amino groups which are located at the ends of the conjugated bonds which cause the color of the system. The influence of the substituents which are found within this system and facilitate or hinder electron displacement in the conjugated chain has also been studied. Thus, for example, the introduction into the benzene nucleus of the malachite green molecule of electron acceptor substituents [2], particularly of nitro groups, evokes deepening of the color; electron donor substituents on the contrary, evoke diminution of the color.

The influence of substituents has been studied to a lesser extent in the series of hydroxyfuchsones dyes. The subject of the present investigation was primarily the color of alkaline solutions of benzaurin derivatives, in particular of indicators of the sifonaphthalein type.

Hydroxyfuchsones dyes, which are colored yellow in the non-ionized state, form deeply colored ions not only in an alkaline, but also in a strongly acidic medium [3]. This permits us to study the dependence of the color of the hydroxyfuchsones on the character of the ionization, and also the influence of substituents on the change of the color in various media, which should be of distinct interest from the point of view of the problem of the association between structure and color of colored substances.

A very convenient object of investigations in this connection is the methoxy-derivative of the hydroxyfuchsones, in which the presence of methoxy groups [4] considerably deepens the color of the dyes in alkaline and particularly in strongly acidic media. This increases the practical significance of the dyes and facilitates the study of their color in various media.



After having prepared the hitherto unknown nitro and halogeno derivatives of 3,3'-dimethoxybenzaurin [5, 6], we were able to study the influence of nitro groups introduced into the benzene nucleus on the color in neutral solvents, in strongly acid and in alkaline medium. The color carriers under the conditions were: the dye in the non-ionized state (a), the onium cation of the dye (b), and the anion of the dye (c).^{*} This investigation was preceded by

^{*} All the formulas given are for unsubstituted 3,3'-dimethoxybenzaurin.

the study of the influence of the nitro group and halogens on the indicator properties of the dyes, described in another communication [1].

The determination of the color was carried out on an automatic State Optics Institute spectrophotometer, which consisted of a double monochromator in conjunction with a photometric layout that ensured a very accurate automatic recording of the transmission curve. We carried out the photomeasurements in the visible portion of the spectrum in the 400-700m μ range at an aperture width of 4 m μ .

The determination of the color of the dyes in the non-ionized state was carried out in a 0.0001 N solution of the dye in twice redistilled ethyl alcohol. The absorption curves are depicted in Figs. 1, 2, and 3.

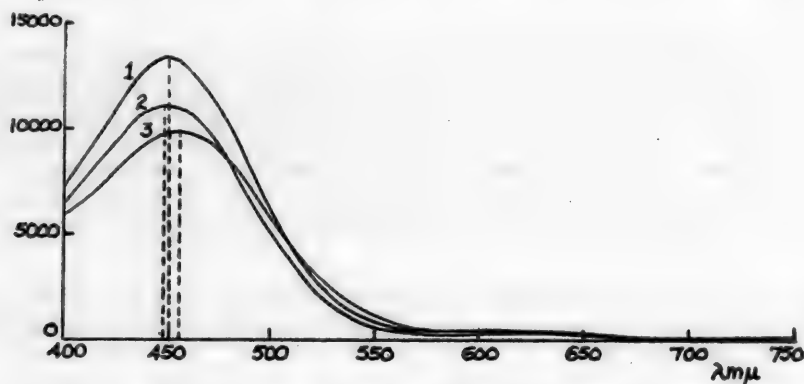


Fig. 1. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO₂; 3) p-NO₂.

Comparison of the curves shows that they have a completely identical character. The presence of nitro groups and halogens only insignificantly displaces the color of the dyes in the non-ionized state. The dependence of the degree of the displacement of the absorption maximum on the position of the halogen is clearly noticeable. The o-halogen derivatives are most highly colored. The character of the halogen plays a small role. The opposed influence of halogen in the p- and in the m-positions is striking.

We also studied the dependence of the color of the dye in the non-ionized state on the character of the solvent. With this object, we determined the absorption spectra of 3,3'-dimethoxybenzaurin in benzene, ethyl alcohol and glacial acetic acid. The absorption curves are set forth in Fig. 4.

As is evident from Fig. 4, the absorption curves differ both as regards structure and as regards position of the maximum. The solution of the dye in benzene is considerably more highly colored than in alcohol and in acetic acid, which, evidently, is associated with the polarity of the solvent. Analogous results were detected [7] during the study of the color of indophenol blue in benzene, alcohol and acetic acid. The positions of the absorption maxima of solutions of 3,3'-dimethoxybenzaurin and indophenol blue in various solvents are set forth in Table 1 for comparison.

TABLE 1

Solvent	3,3'-Dimethoxybenzaurin		Indophenol blue	
	position of the maximum (m μ)	displacement (m μ)	position of the maximum (m μ)	displacement (m μ)
Benzene	416		577	
Alcohol	451	+35	606	+29
Glacial acetic acid	455	+39	610	+33

Determination of the color of the cations (type b) was carried out in 0.00005 N solution of the dye in 15% hydrochloric acid. The absorption curves are given in Figs. 5, 6, and 7. It is evident from the figures that all the curves are similar in form, and in addition to the principal maximum, have an additional maximum in a region close to the ultra-violet portion of the spectrum, while for some dyes it passes over into this portion of the spectrum.

The presence of the nitro group, particularly in the p-position, causes the greatest bathochromic effect. With the halogen derivatives, the color is deepened in proceeding from the p-substituted to the m-substituted and

particularly, to the o-substituted derivative. In all cases, the bromine derivatives were colored somewhat more deeply than the corresponding chloro derivatives.

We simultaneously studied the dependence of the color of onium cations on the character of the anion of the acid. Previously [4], in comparing the absorption spectra of solutions of 3,3'-dimethoxybenzaurin in hydrochloric and sulfuric acid with a Kōning-Martens spectrophotometer we did not find any difference between them. With the use of the more completely automatic GOI spectrophotometer, it was established that the character of the acid has some influence on the absorption spectrum of the cation formed. The absorption curves of a solution of 3,3'-dimethoxybenzaurin in 15% hydrochloric acid, in 33% sulfuric acid, in 10 and 72% perchloric acid and in 45% trichloroacetic acid are given in Fig. 8.

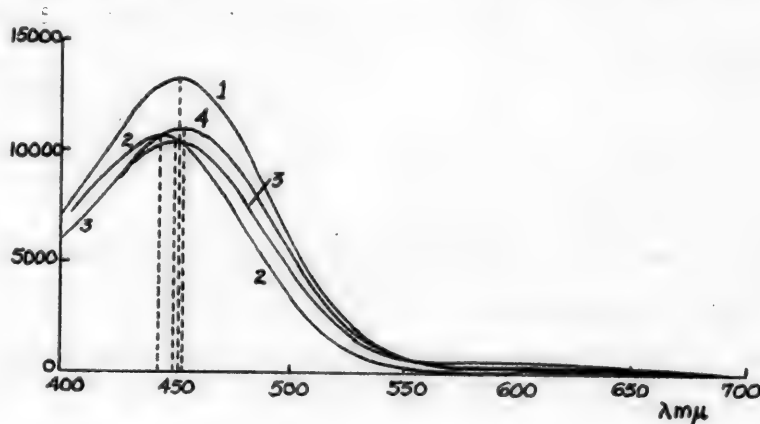


Fig. 2. 1) 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl.

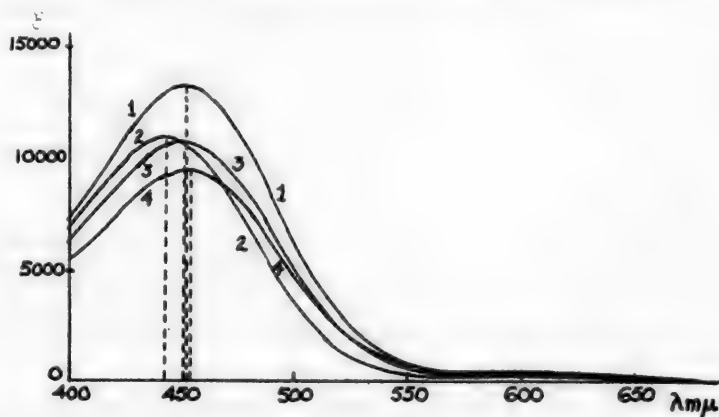


Fig. 3. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

Fig. 8 shows that in all cases, with the exception of the solution in trichloroacetic acid, the absorption spectra are identical in form and differ in the position of the absorption maxima. The solutions in sulfuric acid and in perchloric acid are somewhat more highly colored than that in hydrochloric acid. The displacement of the maximum for the solution in sulfuric acid reaches 2 mμ, while for 10% perchloric acid, it reaches 12 mμ. Trichloroacetic acid causes a deepening of the color with change in the character of the absorption curve.

The determination of the color of dye anions of type (c) was carried out in a borate buffer with a pH of 9.5. The absorption curves are set forth in Figs. 9, 10, and 11.

All these curves are identical in form, having one principal maximum in the visible portion of the spectrum and a marked supplementary maximum in the ultraviolet. Only with the o-halogen derivatives did the supplementary maximum appear in the region adjoining the ultraviolet portion of the spectrum.

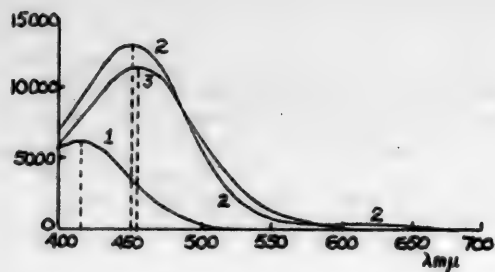


Fig. 4. 1) Benzene; 2) ethyl alcohol; 3) glacial acetic acid.

In alkaline solution, the presence of a nitro group in the p-position causes a maximum bathochromic effect. A nitro group in the m-position causes deepening of the color to a lesser extent. The introduction of halogens also leads to deepening of the color, and the extent of the deepening increases as one proceeds from p-substituted to m-substituted and to o-substituted derivatives. The bromo-derivatives in alkaline solutions are also colored more deeply than the corresponding chloroderivatives.

The positions of the chief absorption maximums of solutions of nitro and halogen derivatives of 3,3'-dimethoxybenzaurin in strongly acid and in alkaline media and the displacements of the maxima in comparison with solutions of unsubstituted 3,3'-dimethoxybenzaurin are compared in Table 2.

TABLE 2

Substituent	H	p-NO ₂	m-NO ₂	p-Cl	m-Cl	o-Cl	p-Br	m-Br	o-Br
Position of the maximum in acid medium (mμ)	544.5	572.5	563.5	548.5	554	564	549	554.5	564.5
Displacement of the maximum (mμ)	0	+28	+19	+4	+9.5	+19.5	+4.5	+10	+20
Position of the maximum in alkaline medium (mμ)	594	612.5	605.5	598.5	600.2	603	599.5	601	604
Displacement of the maximum (mμ)	0	+18.5	+11.5	+4.5	+6.2	+9	+5.5	+7	+10

It is evident from the data of Table 2 that nitro groups and halogens cause the regular bathochromic effect in all cases. It is manifested to the greatest extent by the nitro group which has manifestly electron acceptor properties, particularly when it is present in the p-position of the benzene nucleus. The halogens, which have a dual electron influence, evoke the bathochromic effect to a lesser extent. It is most strongly expressed in the o-halogen derivatives.

The nitro group and halogens exert an analogous influence on the color of the basic triphenylmethane dyes. This is visible at a glance from Table 3, in which the absorption maxima of malachite green and certain of its derivatives which contain the nitro group and halogens in the benzene nucleus are indicated [8].

TABLE 3

Substituent	H	p-NO ₂	m-NO ₂	o-NO ₂	o-Cl
Position of the maximum (mμ)	616	637.0	635.7	633.1	630.1
Displacement of the maximum (mμ)	0	+21	+19.7	+17.1	+14.1

Similar results were obtained during the study of the influence of substituents introduced into the benzene nucleus, on the color of dyes in alkaline solutions. Sulfophthalein, which contains the sulfo group in the o-position of the benzene nucleus, is more deeply colored than benzaurin, and the maximum is displaced by +6 mμ; for m- and o-bromobenzaurins the absorption maximum is also displaced by +12 and +15 mμ [9].

It is evident from what has been set forth above that in all cases involving the introduction into an unsubstituted benzene nucleus of dyes of the malachite green and benzaurin group of electron acceptor substituents, their influence leads to deepening of the color; our new experiments indicate that for hydroxyfuchsones dyes of the benzaurin

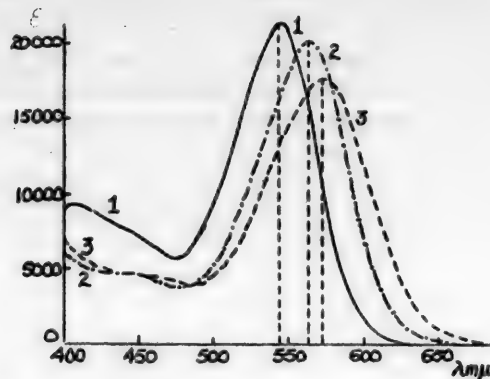


Fig. 5. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO₂; 3) p-NO₂.

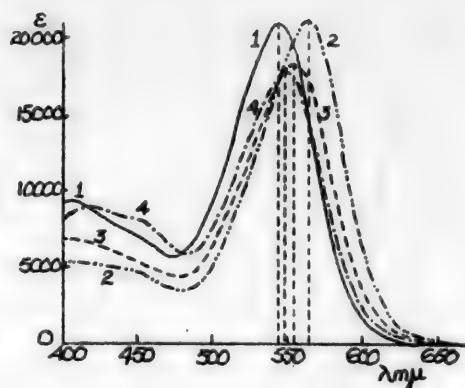


Fig. 6. 1) 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl.

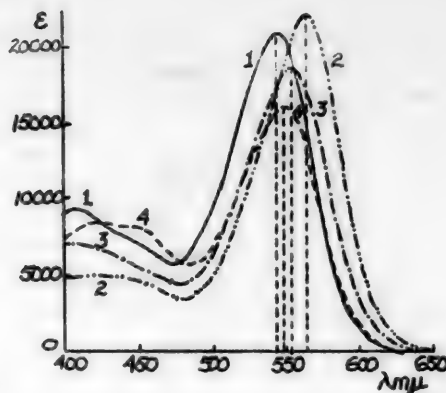


Fig. 7. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

group such an influence is manifested both in strongly acid and in alkaline medium, to a greater extent for onium cations and to a lesser extent for anions of the dyes.

It is also evident from Table 2 that both for unsubstituted 3,3'-dimethoxybenzaurin and for its nitro and halogen derivatives, the color of the anions of the dye is considerably deeper than the color of the onium cations. To explain this, Ioffe [10] put forward the hypothesis that in the anion of the dye, the color is due to oscillations of the

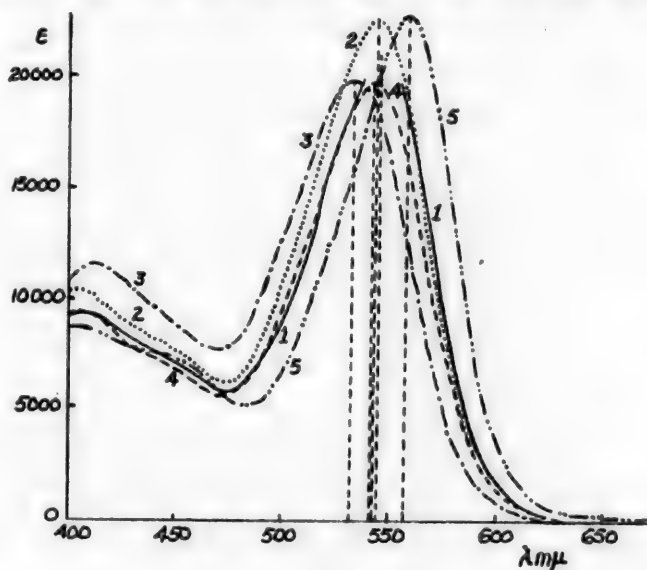


Fig. 8. 1) 15% hydrochloric acid; 2) 33% sulfuric acid; 3) 10% perchloric acid; 4) 72% perchloric acid; 5) 45% trichloroacetic acid.

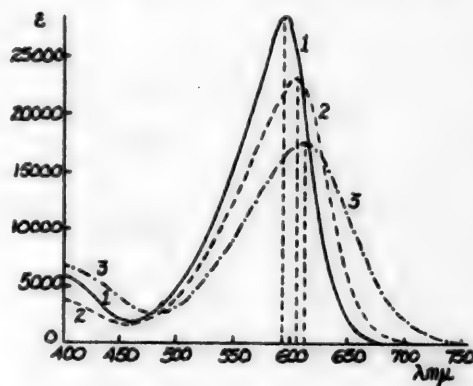


Fig. 9. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO₂; 3) p-NO₂.

electric charge between the terminal oxygen atoms along all the conjugated chain found between them. In the cation of the dye the migration of a positive charge is possible along the lesser conjugated chain, since in its center is located the triphenylmethane carbon atom with higher cationotropic properties than in the

case of the oxygen atom. In the light of these considerations, one can understand in principle the fact that the presence in the benzene nucleus of electron acceptor groups which strengthen the cationotropic character of the central carbon atom, exerts a greater bathochromic effect on the color of the said cations of the dyes, and to a lesser extent on the color of their anions.

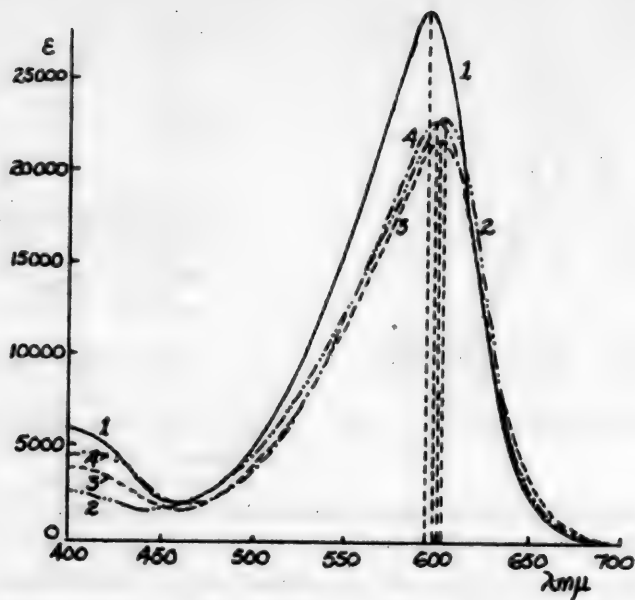


Fig. 10. 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl.

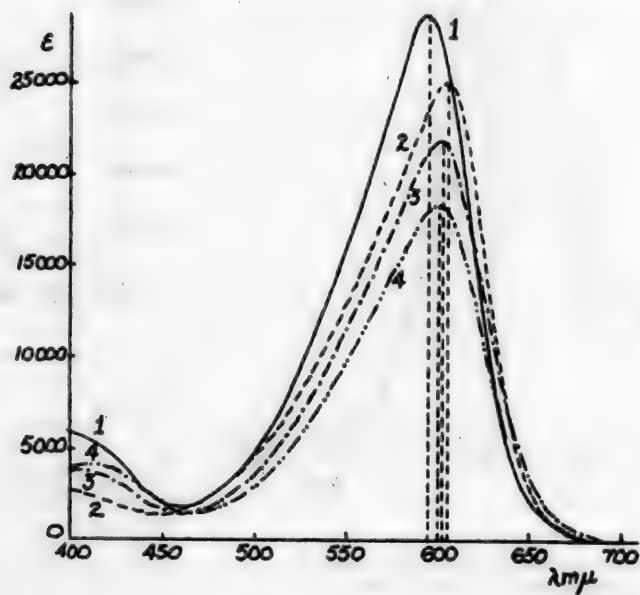


Fig. 11. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

SUMMARY

The influence of substituents on the color of derivatives of 3,3'-dimethoxybenzaurin which contain nitro groups and halogens in the benzene nucleus was studied. It was established that the presence of these substituents influences the color of the dyes in the non-ionized state while in the ionized state, only in strongly acidic and alkaline solutions. Nitro groups and halogens also cause deepening of the color of the onium cation of the dye in strongly acid solution, and of the anion of the dye in alkaline solution. The greatest bathochromic effect is caused by the nitro group in the p-position to the central carbon atom. The bathochromic influence of halogens increases step by step as one proceeds from the p-position to the m-position and to the o-position. The bromoderivatives are colored somewhat more deeply than the corresponding chloroderivatives.

The anions of all the dyes studied are considerably more deeply colored than the onium cations. The bathochromic influence of electron acceptor substituents is manifested to a greater extent in the cations of the dye.

It was also shown that the color of hydroxyfuchson dye, both in the non-ionized state and in the form of onium cations, depends on the character of the solvent.

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* See Consultants Bureau Translation, page 349.

** See Consultants Bureau Translation, page 1163.

*** See Consultants Bureau Translation, page 1597.

**** See Consultants Bureau Translation, page 2051.



CARBOXYLIC ANHYDRIDES OF AMINO ACIDS AS STRUCTURAL FRAGMENTS

IN THE PROTEIN MOLECULE. II.

L. N. Akimova and N. I. Gavrilov

In the preceding communication [1] we showed not only the reality of the existence of carboxylic anhydrides of amino acids, but also a method for synthesizing them. Fränkel showed in his time [2] that amino acid anhydrides can be formed synthetically by the trypsin system, which permits us to consider their structure as presumptively "natural". Attempts to investigate the behavior of these anhydrides depending on the presence of enzymes at various concentrations of hydrogen ions were not successful. Evidently, this was a consequence of the fact that the simplest anhydrides selected by us, those of glycine and alanine, could not be compared with such anhydrides as those of tryptophane or of tyrosine. It is precisely these latter amino acids which are most labile bound in the molecule and are of interest for the structural chemistry of protein. None-the-less, our experiments, carried out with the simplest anhydrides of glycine, shed light both on the relation of these anhydrides to the enzymes and on their stability in relation to the alkalinity of the substrates. The study of the behavior of carboxylic anhydrides in acid medium in the presence of enzymes showed a tendency toward the pepsin fermentation of these structures. The great instability of these anhydrides to high values of hydrogen ion concentration was clearly shown. This all the more underlined the necessity of studying enzymatic processes which proceed both in the direction of synthesis of the carboxylic anhydride bond and of its hydrolysis.

Attempts to prepare tyrosine or tryptophane anhydrides synthetically have not yet been successful. Nevertheless, by the study of these systems one can evidently proceed to the solution of this problem, extraordinarily important in connection with the problem of protein structure.

EXPERIMENTAL

1. Synthesis of Carbobenzoxytyrosine Anhydride

0.75 g of carbobenzoxytyrosine, prepared by Bergmann's method [3], was dissolved in 10 ml of absolute dioxane. (N-Carbenzoxytyrosine is very excellently soluble in dioxane, alcohol and acetone). 0.4 ml of isobutyldimethylamine and 0.4 ml of chlorocarbonic ester were then added. After 10 minutes, the initially transparent solution markedly thickened (without evolution of CO_2). After having added 0.75 g more of carbobenzoxytyrosine in 10 ml of absolute dioxane, we left the reaction mixture overnight. No visible changes occurred. The precipitate was filtered off, washed repeatedly with dioxane and then with ether. The substance after having been dried in a vacuum desiccator melted at 156° and did not manifest any of the initial carbobenzoxytyrosine. The qualitative reaction with Millon's reagent was negative. It was assumed that the mixed anhydride of carbobenzoxytyrosine (at the phenolic hydroxyl group) and chlorocarbonic ester was formed. The unreacted carbobenzoxytyrosine was isolated from the dioxane filtrate.

2. Fermentation of Carbobenzoxyalanine Anhydride by Gastric Juice

a) The activity of the gastric juice was verified on a 2% aqueous gelatin solution.

b) 10 ml of 0.36% hydrochloric acid and 5 ml of gastric juice (active) were added to 0.5 ml of carbobenzoxyalanine anhydride. After having stood for 24 hours in a thermostat at a pH of 1, 0.25g of the initial anhydride was recovered and, after the filtrate had been concentrated, 0.15 g of carbobenzoxyalanine was isolated. The extent of the decomposition amounted to 30%.

c) 10 ml of 0.36% hydrochloric acid (without enzyme) was added to 0.1 g of carbobenzoxyalanine anhydride. After having stood for 24 hours in a thermostat, 0.07 g of the initial anhydride was recovered; there were traces of carbobenzoxyalanine in the filtrate. 30% hydrolyzed.

Thus, the decomposition of carbobenzoxyalanine anhydride described in experiment "b" amounts to its hydrolysis by 0.36% hydrochloric acid.

3. Fermentation of Carbobenzoxyglycine Anhydride by Gastric Juice

a) The activity of the gastric juice was verified on a 2% gelatin solution.

b) 10 ml of 0.36% hydrochloric acid and 5 ml of active gastric juice were added to 0.7 g of carbobenzoxyglycine anhydride. After standing for 6 hours in a thermostat at 37°, 0.2 g of the initial anhydride was recovered. The extent of the decomposition was equal to 71.4%.

c) 15 ml of 0.36% hydrochloric acid without enzyme was added to 0.7 g of the same anhydride. After standing for 6 hours at 37°, 0.18 g of the anhydride was recovered. 74.2% of the anhydride was hydrolyzed.

Thus, carbobenzoxyglycine anhydride is not fermented by gastric juice, but is decomposed under the influence of 0.36% hydrochloric acid for 6 hours at 37° to the extent of 72.5% (mean value of the quantities from experiments "b" and "c").

4. Fermentation of Carbenzoxyglycine Anhydride by Trypsin

a) The activity of trypsin was verified on a 5% aqueous solution of Witte peptone.

Experiment 1. 1 ml of a 2% trypsin solution was added to 10 ml of a solution of Witte peptone. After it had stood for 6 hours in a thermostat, the solution was titrated by the Sørensen-Gavrilov method. 4.0 ml (0.15 ml in the control) of 0.2 N NaOH was consumed in the titration. 3.2 ml of 0.2 N NaOH should have been consumed theoretically. The activity of the enzyme was insignificant and was expressed in an increase in the amine groups amounting to 0.65 ml of 0.2 N NaOH.

Experiment 2. 1 ml of a 2% solution of trypsin was added to 10 ml of a solution of Witte peptone. After it had stood for 6 hours at 37° the solution was titrated by the Sørensen-Gavrilov method. 7.8 ml (0.15 ml in the control) of 0.2 N NaOH was used up in the titration. Theoretically, 3.8 ml of 0.2 N NaOH should have been consumed in the titration. The increase equal to (7.8 - 0.15 - 3.8 ml) 3.85 ml of 0.2 N NaOH showed the greater activity of this enzyme in comparison with the enzyme of Experiment 1.

b) Fermentation of carbobenzoxyglycine anhydride with trypsin in a phosphate buffer. Experiment 1 (with enzyme). 25 ml of 1/15 molar solution of buffer mixture (0.51 g of Na_2HPO_4 and 0.26 g of NaH_2PO_4) and 2 ml of a 2% trypsin solution were added to 1 g of carbobenzoxyglycine anhydride. After it had stood for 6.5 hours in a thermostat, the solution was rendered strongly acidic and 0.85 g of Na_2HPO_4 was then added. 6.5 hours after the addition of Na_2HPO_4 (in the thermostat) the precipitate was filtered off, washed on the filter with water, alcohol and ether. The precipitate obtained (0.15 g) consisted of unreacted carbobenzoxyglycine anhydride. The neutral filtrate was concentrated in a vacuum to small volume and then was acidified with hydrochloric acid to an acidic reaction. The precipitate which thereupon settled out was filtered off and washed on a filter with water. The yield of dried substance amounted to 0.55 g. According to the melting point (121°), the substance consisted of carbobenzoxyglycine [3]. Thus, 85% of the carbobenzoxyglycine anhydride decomposed.

Experiment 2 (without enzyme). 12.5 ml of 1/15 molar phosphate buffer was added to 0.5 g of carbobenzoxyglycine anhydride. After standing 6.5 hours in a thermostat at 37° a strong acidification of the medium (pH 4) was observed. 0.42 g of Na_2HPO_4 was added to the solution and left to stand in a thermostat for 6.5 hours more. The precipitate was filtered off and proved to be the initial anhydride. Its weight was equal to 0.07 g which amounted to 14% of the carbobenzoxyglycine anhydride taken for the reaction. The neutral filtrate was concentrated in a vacuum to small volume and after acidification, the carbobenzoxyglycine was isolated.

Thus, 85% of the carbobenzoxyglycine anhydride is hydrolyzed by the action of trypsin in the course of 13 hours at 37° under the optimal conditions for its action (phosphate buffer and without it).

5. Fermentation of Carbenzoxyglycine Anhydride by Pepsin

a) The activity of pepsin was verified on a 2% aqueous gelatin solution. Merck brand pepsin proved to be the most active of the three pepsins investigated.

b) 10 ml of 1% hydrochloric acid and 0.15 mg of active pepsin were added to 1 g of carbobenzoxyglycine anhydride. After standing for 22 hours in a thermostat, the precipitate was filtered off and repeatedly washed with water and alcohol. The weight of the substance after having been dried in a vacuum desiccator was 0.41 g, which amounted to 41% of the anhydride taken in the reaction. Thus, 59% of the carbobenzoxyglycine anhydride was decomposed. Carbenzoxyglycine was isolated from the filtrate.

c) 10 ml of 1% hydrochloric acid (without enzyme) was added to 1 g of the carbobenzoxyglycine anhydride. After standing for 22 hours in a thermostat at 37°, 0.42 g of the initial anhydride was recovered in the manner described above. The percentage of hydrolysis of the carbobenzoxyglycine anhydride amounted to 58% in this case.

It undoubtedly follows from the data of experiment "b" that the decomposition of carbobenzoxyglycine anhydride proceeds as a result of its hydrolysis by 1% hydrochloric acid.

6. Verification of the Synthesizing Capacity of Gastric Juice (Pepsin) on Carbobenzoxyglycine Anhydride

0.1 g of glycine in 5 ml of water and in 2.75 ml of 0.2 N NaOH, and 5 ml of 2% pepsin solution (pH of the medium 4.7) were added to 0.5 g of carbobenzoxyglycine anhydride. After standing for 24 hours in a thermostat, 0.2 g of the initial anhydride was recovered from the solution while 0.2 g of carbobenzoxyglycine was isolated from the filtrate. If the synthetic reaction of the formation of carbobenzoxyglycine glycine (dipeptide) had occurred from the carbobenzoxyglycine anhydride and the glycine, then this dipeptide should have been found by its isolation in the mixture with carbobenzoxyglycine, in view of their close solubility. However, investigation of the carbobenzoxyglycine (negative biuret reaction, absence of melting point depression with synthetic carbobenzoxyglycine) showed that the formation of dipeptide does not occur in this case.

TABLE

Comparative Stability of Carbobenzoxyglycine Anhydride as a Function of the Hydrogen Ion Concentration at 37°

Enzymatic system	Duration of the action (in hrs.)	Decomposition (in %)
Gastric juice + 0.36% HCl	8	72
0.36% hydrochloric acid	6	72.5
Trypsin (phosphate buffer)	13	85
Phosphate buffer	13	85
Pepsin + 1% HCl	22	58
1% Hydrochloric acid	22	58

SUMMARY

1. In an attempt to obtain the mixed anhydride of carbobenzoxytyrosine and chlorocarbonic ester, the reaction proceeded at the phenol hydroxyl group.

2. In the trypsin and pepsin enzyme systems, enzymes which hydrolyzed the carboxyl anhydride bond were not detected (in the case of carbobenzoxyglycine anhydride).

3. The hydrolysis of glycine carboxylic anhydride proceeds most readily of all in alkaline medium and is retarded in the acid zone.

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ON THE STRUCTURE OF GRAMICIDIN C

I. REDUCTION OF GRAMICIDIN C

P. G. Ioanisiانی, N. I. Gavrilov and M. I. Plekhan

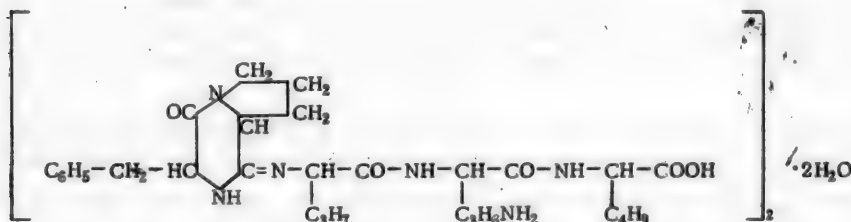
As yet, the structure of gramicidin C cannot be considered as established [1-7]. The hypothesis that its structure is that of a cyclopenta- or of a cyclodecapeptide is improbable since such ring compounds are evidently not encountered in nature. Attempts to synthesize similar ring compounds must be considered unsuccessful up to the present time.

The representation of gramicidin C as a common penta- or decapeptide has not proved correct, since synthetic peptides of such a structure have turned out to be slightly active antibiotically and, in contrast to gramicidin C, have an α -amino and carboxyl group.

Of the numerous properties of gramicidin C it is necessary to point out the following.

1. The solubility of the antibiotic in alcohol, acetone and chloroform, which is uncharacteristic of linear peptides.
2. The absence of free amine groups (except the δ -amine group of ornithine) and the practical impossibility of determining free carboxyl groups.
3. The dimer character of the gramicidin C molecule which was shown by one of us [7].

The indicated properties of gramicidin C permit one to seek its structural analogy with protein fragments. We, therefore, assume that gramicidin C has the structure of a dimer monoamidine:



Such a structure explains a number of its properties. The basic group of such amidines is not determined either by Sørensen's nor by Van Slyke's nor by Wiltstätter's methods. The solubility of amidines in organic solvents is also great.

In alcoholic solution with alkali and CuCl_2 , gramicidin C forms a violet colored biuret complex with an absorption maximum at a wave length of 570 $\text{m}\mu$ (this reaction proceeds considerably more difficultly in aqueous medium). The character of the absorption in the visible portion and the position of the maximum argue in favor of the fact that the polypeptide chain in the structure of gramicidin C is limited and contains three amino acid radicals [8]. During prolonged standing, the biuret complex of gramicidin C undergoes change - the violet color is converted into a bright raspberry color. The absorption maximum is strongly displaced toward the short wave side and is located in the 540 $\text{m}\mu$ region, which argues in favor of the appearance in the structure of a longer chain [8]. These observations on the biuret complex of gramicidin C are quite well explained by the structure assumed above.

Gramicidin C also gives an anhydride reaction with picric acid, which indicates the presence in its molecule of a piperazine ring.

The following peptides were isolated from the incomplete hydrolyzate of gramicidin C [3]: valyl-ornithine, ornithyl-leucine, leucyl-phenylalanine, phenylalanyl-proline, valyl-ornithyl-leucine, phenylalanyl-prolyl-valine,

prolyl-valyl-ornithine. Thus, the following sequence of aminoacids in the gramicidin C molecule was established: phenylalanyl-propyl-valyl-ornithyl-leucyl.

Such a sequence fits into the structural formula assumed by us. Phenylalanine and proline apparently enter into the composition of the diketopiperazine type ring. The indicated amino acids are characterized by the fact that they readily form diketopiperazine rings.

The dimerization of the monoamidine can proceed according to two patterns:

1) according to Sedgewick-Syrkin-Shigorin. However, the formation during hydrolysis of the dipeptide leucyl-phenylalanine would then become incomprehensible. Further, such a dimerization should evoke the disappearance of the basic properties in the amidine group and the appearance of acidic properties in the freed carboxyl groups;

2) with the formation of an autoacylated dimer. Such an acylated amidine was studied by one of us with Akimova [9].

We shall return to the proof of the structural formula assumed by us for gramicidin C in the future. In the present work, we employed the method of electroreduction proposed by one of us with Koerina [10] to demonstrate the said structure. This method was refined by us. The gasometric determination of amine nitrogen, by Van Slyke's method, was carried out in a new apparatus proposed by one of us [12]. Potentiometric titration with a glass electrode was employed in the Sørensen micromethod. We carried out the electroreduction with a rotating mercury electrode.

EXPERIMENTAL

Gramicidin C was recrystallized from ethyl alcohol and dried in a vacuum desiccator over sulfuric acid. The substance melted at 281°.

Found %: C 55.31; H 8.04; N 13.21; Cl 4.96. $C_{30}H_{48}O_7N_5 \cdot HCl \cdot 2H_2O$. Calculated %: C 56.01; H 7.99; N 13.08; Cl 5.51.

The moisture content (determination was carried out in a drying chamber at 105°) was 2.67%.

The amine nitrogen in gramicidin C was determined gasometrically (15 minutes) and by formol potentiometric titration. The complete hydrolysis of the antibiotic was carried out with concentrated hydrochloric acid. In the hydrolyzate the total nitrogen by Kjeldahl's method was determined, and also the amine nitrogen gasometrically and by formol potentiometric titration. The aqueous solutions of gramicidin C and its hydrolyzate were investigated analogously.

The methods of analysis were worked out by one of us. The gasometric determination of the amine nitrogen was carried out in a new apparatus (micromethod) for 15 minutes (it requires 30 minutes in a Van Slyke apparatus).

The formol titration was carried out potentiometrically with the use of a glass electrode. The micromethod was verified for a number of aminoacids and for artificial mixtures of them. The titration was carried out in a pH range 7.0-9.0. However, it was later established with amino acid mixtures that it was necessary to carry out such titration in the 6.0-9.0 pH range.

The electroreduction of gramicidin C was carried out with a mercury cathode by the method which was described previously [7, 11], but with minor changes. The current density was 56 mA/cm². 50% acetic acid, to which concentrated hydrochloric acid was added for better conduction of the electrical current (40 ml HCl was added to 200 ml of 50% CH₃COOH), served as the cathode solution. The gramicidin C was dissolved in glacial acetic acid. The solution obtained, together with the wash water, was introduced into the cathode cell, after which the hydrochloric-acetic solution was added. The volume of the cathode solution was equal to 200-210 ml. The anode solution consisted of 10% hydrochloric acid. About 100 mg of the antibiotic was taken for the electroreduction. The temperature of the cathode solution was held in the 15-25° range. The duration of the electroreduction was equal on the average to 7 hours. With the object of verifying and confirming the results obtained, two parallel experiments were set up with equal samples of gramicidin C.

The course of the further treatment of the catalyzate consisted of the following. Acetic acid, water and the hydrochloric acid residue were distilled off in a water jet pump vacuum at a water bath temperature which did not exceed 30-35°.

After completion of the distilling off of the solvent, and with the object of more complete elimination of the hydrochloric acid, about 10 ml of distilled water was added three times to the dry residue and each time the

distillation was renewed until complete elimination of the water added had occurred. The reduced gramicidin C was then dissolved in distilled water and the solution obtained together with wash water was transferred to a 25 ml measuring flask, after which the analysis indicated above was carried out. The solution of reduced antibiotic yielded a biuret reaction. The reaction with picric acid was negative.

In other experiments, complete hydrolysis of the reduced gramicidin C was carried out after electroreduction and distilling off the solvent. The total nitrogen was determined in the hydrolyzate by Kjeldahl's method and also the amine nitrogen gasometrically and by formol potentiometric titration. The hydrolyzate gave a negative biuret reaction and a negative reaction with picric acid.

It should be noted that the reduced gramicidin C was very excellently soluble in distilled water and concentrated hydrochloric acid, while gramicidin C is not soluble in them.

The complete hydrolysis of reduced and non-reduced antibiotic was carried out with concentrated hydrochloric acid for 39 hours in a round-bottom flask supplied with a reflux condenser. The flask was placed in a glycerine bath, the temperature of which was 115-125°.

The results of the electroreduction of gramicidin C are set forth in Table 1.

TABLE 1

Analysis of the Nitrogen Distribution of Gramicidin C Hydrochloride

Conditions of the experiment	Total nitrogen (in % of the sample)	Amine nitrogen as determined by formol titration		Amine nitrogen, determined gasometrically (15 minutes)	
		in % of the sample	in % of the total nitrogen	in % of the sample	in % of the total nitrogen
Gramicidin C prior to electroreduction and prior to hydrolysis	13.35	1.58	11.83	2.04	15.27
Gramicidin C prior to electroreduction and after hydrolysis	13.50	11.23	84.12	11.06	82.84
Gramicidin C after electroreduction and prior to hydrolysis	13.24	5.71	42.77	4.69	35.13
Gramicidin C after electroreduction and after hydrolysis	13.26	8.66	64.87	8.91	66.74
Diminution of the amine nitrogen in the hydrolyzates prior to and after electroreduction	—	2.57	19.25	2.12	16.10

Distribution chromatography on paper gave the following results:

- 1) Complete hydrolysis: ornithine, valine, leucine, phenylalanine (proline masked by valine);
- 2) after reduction, only a spot was detected which was hardly displaced;
- 3) complete hydrolysis after reduction (three spots): valine, leucine, ornithine (no phenylalanine; proline was absent or masked by valine).

The chromatograms confirmed our scheme for the structure of the gramicidin monomer.

In considering the formol titration data it should be noted that the figures for amine nitrogen turned out to be rather low, as a consequence of the incorrect selection of the pH range during titration (7.0-9.0). It was later established that it is necessary to carry out the titration at a pH of 6.0-9.0. It was also established that the reduction in the amine nitrogen in the hydrolyzates prior to and after the electroreduction is expressed by figures of the same order of magnitude, independently of whether hydrolyzates from pH 7.0-9.0 or pH 6.0-9.0 were being titrated.

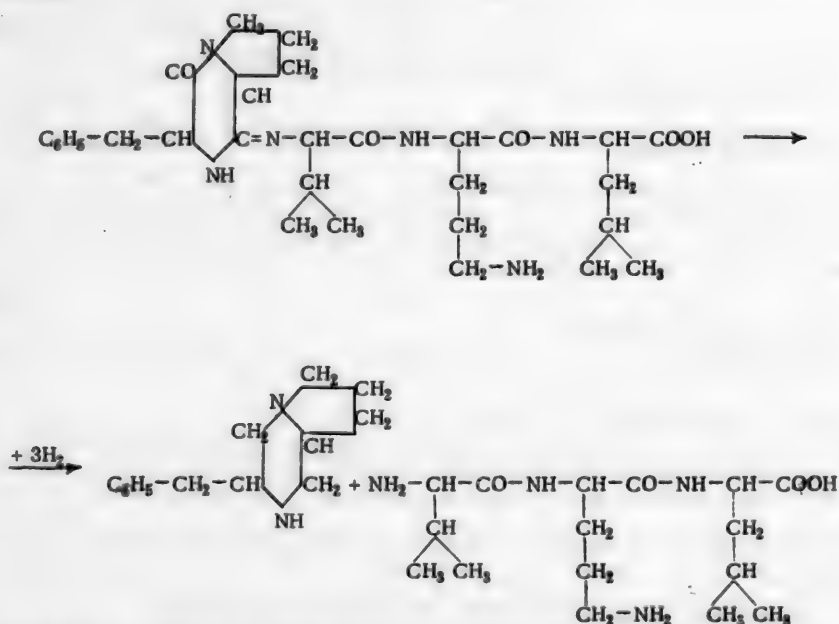
It is evident from the data of Table 1 that 2.04% of amine nitrogen or 15.27% of total nitrogen was found gasometrically in the initial gramicidin C, which is exactly equivalent to the single nitrogen atom of the δ -amino group of ornithine (theoretically, 1 nitrogen atom in gramicidin C would amount to 2.2% or 16.6% of the total nitrogen). 11.06% of amine nitrogen was found in the gramicidin C hydrolyzate. Consequently, of the 6 nitrogen atoms which enter into the gramicidin C molecule, 5 atoms have been determined. This is in complete agreement with the theoretical representations, since proline nitrogen is not determined by Van Slyke's method.

4.69% of amine nitrogen was found in the reduction of gramicidin C, which amounts to 2 nitrogen atoms. One can conclude from a comparison of the data for amine nitrogen of the reduced and non-reduced gramicidin C that after the electroreduction the amine nitrogen is doubled, i.e., after the electroreduction one more amine group can be determined. This is readily explained by the reduction reaction of gramicidin C assumed by us below, in accord with which the reduced antibiotic consists of piperazine and tripeptide fragments. There is one additional free amine group in the tripeptide besides the δ -amine group of ornithine.

8.91% of amine nitrogen, or 66.74% of total nitrogen, which is equivalent to 4 nitrogen atoms, was detected gasometrically in the hydrolyzate of reduced gramicidin C. The reduction in amine nitrogen (in comparison with the hydrolyzate of unreduced antibiotic) was equal to 2.15%, which is equivalent to 1 nitrogen atom. Actually, the hydrolysis of reduced gramicidin C leads to the cleavage of the tripeptide which forms while the acid stable piperazine is not hydrolyzed. Therefore, only 4 nitrogen atoms of the 6 nitrogen atoms in the hydrolyzate of reduced gramicidin C should be determined. This was confirmed by the experimental data. It should be noted that these considerations apply only if one assumes that proline enters into the composition of the ring, for in the opposite case, 3 nitrogen atoms should be determined in the reduced hydrolyzate of gramicidin C, i.e., the diminution of amine nitrogen should correspond to 3 nitrogen atoms, which is not actually observed.

The diminution of amine nitrogen, determinable by formol titration in the reduced hydrolyzate, is equal to 2.57% in comparison with the unreduced hydrolyzate, which also corresponds to 1 nitrogen atom. The data of the formol titration are in agreement with our assumptions concerning the structure of gramicidin C. It is only necessary to bear in mind that 50% of the piperazine is titrated by Sørensen's method [10], i.e., 1 of the 2 nitrogen atoms is determined.

Thus, the process of electroreduction of gramicidin C proceeds in the following manner:



The biuret reaction of gramicidin C was carried out under the following conditions: 0.1052 g of gramicidin C was dissolved in 14 ml of alcohol and 0.7 ml of 5 N NaOH and several drops of saturated CuCl_2 solution (to a volume of 15 ml) were added to the solution. After 2.5 hours, the excess Cu(OH)_2 was filtered off and the deep violet solution of the complex was measured spectrophotometrically with a Kollman apparatus (Table 2). The light absorption maximum was at $\lambda = 570 \text{ m}\mu$. After the solution had been further kept for 35 days, a gradual change in the color was observed; it was converted into a bright raspberry color. Spectrophotometric measurement of the solution (ϵ_{II}) showed that the absorption maximum was displaced toward the short wave side.

TABLE 2

Optical Density of Copper Complexes of Gramicidin

λ	Concentration of the solution 0.56%		λ	Concentration of the solution 0.56%	
	ϵI	ϵII		ϵI	ϵII
460	0.183	0.416	580	0.698	0.560
480	0.250	0.552	600	0.640	0.415
500	0.358	0.678	620	0.568	0.310
505	—	0.710	640	0.500	0.255
510	0.422	0.740	660	0.438	0.199
540	0.610	0.790	700	0.355	0.178
550	0.665	0.745	730	0.289	0.170
560	0.699	0.689	750	0.950	0.140
570	0.708	0.690			

SUMMARY

The presence in gramicidin C of two diketopiperazine and tripeptide fragments was shown; proline was present in the first. The following peptides were in the incomplete hydrolysis products of gramicidin C: phenylalanyl-proline, phenylalanyl-prolyl-valine; consequently, phenylalanine was present in the diketopiperazine. Thus, the structural formula of the monomer of gramicidin C must be depicted as (prolyl-phenylalanyl)-2-valyl-ornithyl-leucine-amidine.

Nevertheless, for final conclusions concerning the structure of gramicidin C further investigations are necessary, in particular the isolation and identification of the hypothetical piperazine from the reaction mixture after the electroreduction is necessary. The problem of the structure of gramicidin C will be finally solved only after its synthesis.

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- * See Consultants Bureau Translation, page 2181.
- ** See Consultants Bureau Translation, pages 341, 635, 641, 899.
- *** See Consultants Bureau Translation, page 1675.
- **** See Consultants Bureau Translation, page 2207, 2219.
- ***** See Consultants Bureau Translation, page 349.

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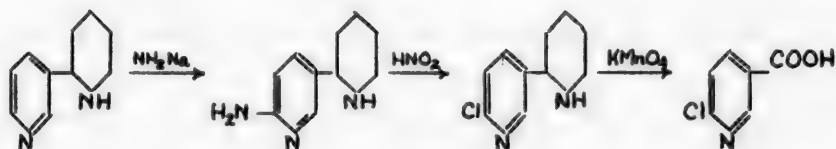
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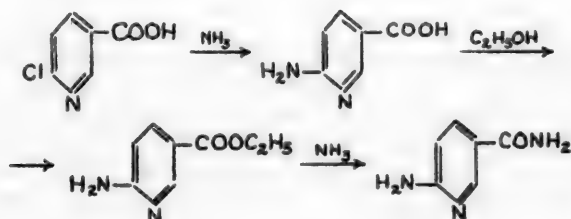
SYNTHESIS OF THE ETHYL ESTER AND AMIDE OF α_1 -AMINONICOTINIC ACID

A. M. Khaletsky and L. Sh. Gurevich

Since the discovery of anabasine by Orekhov [1] many works devoted to the synthesis of derivatives of this alkaloid or products of its degradation [2] have appeared in the literature. The introduction into the pyridine nucleus of anabasine of any substituent represents a possible and rather simple method of obtaining various derivatives of α -pyridinecarboxylic acid by oxidation. Practical experience, however, showed that aminonicotinic acid derivatives were not successfully obtained in satisfactory yields by this method and, therefore, it was necessary to select other synthetic methods, in particular, the substitution of a halogen (chlorine) for the amino group with subsequent oxidation of chloroanabasine and amination of the α_1 -halogen nicotinic acid



During the oxidation of α_1 -chloroanabasine we isolated α_1 -chloronicotinic acid, which was converted by heating with ammonia (in sealed tubes) into α_1 -aminonicotinic acid. By the esterification of the latter with ethyl alcohol the ethyl ester of α_1 -aminonicotinic acid was formed, which on heating with an alcoholic solution of ammonia (in sealed tubes) was converted into the amide of α_1 -aminonicotinic acid according to the scheme



It was found during pharmacological investigation of the ethyl ester of α_1 -aminonicotinic acid* that the latter has anesthetic activity. Since the ethyl ester of nicotinic acid does not possess anesthetic activity, the origin of its anesthetic properties must be ascribed to the introduction of the amino group in the given case.

EXPERIMENTAL

Isolation of Anabasine

a) Isolation of the alkaloids from technical anabasine sulfate by the method of Orekhov and Menshikov [3]. 2.2 kg of alkaloid mixture was obtained from 6 g of technical anabasine sulfate by extraction with ether in the presence of 3.6 kg of 30% potassium hydroxide solution.

b) Separation of anabasine from lupinine. 2.2 kg of the mixture of alkaloids was subjected to vacuum distillation; 1755 g (80% of the total mixture of alkaloids) was thereby distilled at 136-140° (12 mm). The separation of the alkaloids was carried out in three ways: 1) benzoylation of the mixture with subsequent saponification of the benzoylanabasine, 2) nitrosation of the mixture with subsequent decomposition of the nitrosoanabasine, 3) treatment of the mixture of alkaloids with hydrofluosilicic acid with subsequent decomposition of the anabasine fluosilicate. The second method turned out to be the most efficient.

* Carried out by R. S. Konnikova.

600 g of the alkaloid mixture was dissolved in 6 liters of 10% hydrochloric acid and a 14% aqueous solution of sodium nitrite was gradually added to the solution while it was being cooled to 4°. After the addition of 2800 ml of the sodium nitrite solution, the reaction mixture was treated with a 25% potassium hydroxide solution until it had a strongly alkaline reaction; a yellow colored oily liquid thereupon separated out, which was extracted with ether. After drying with roasted sodium sulfate and distilling off the solvent the mixture was subjected to fractional distillation. A fraction with a b.p. of 115-120° (3 mm) initially distilled over. The substance crystallized in the receiving vessel and after recrystallization from petroleum ether melted at 68-69°. A second fraction distilled over at 165-170°. 53.5 g (8.9%) of the first fraction - lupinine - was obtained and 390 g (72%) of the second - nitroso-anabasine.

225 g of the nitrosoanabasine was heated for 3 hours on a water bath with an equal volume of hydrochloric acid (sp. gr. 1.19). After cooling, the liquid was neutralized with 25% potassium hydroxide solution, and the base which was formed was extracted with ether and dried with roasted potash. After distilling off the ether and vacuum distilling at 3 mm, 175.5 g of anabasine (78% in relation to the nitrosoanabasine) was obtained.

0.2146 g sub.: 25 ml 0.0906 N HCl. 10.1 ml of 0.095 N KOH was used up in back titration. Found %: $C_{10}H_{14}N_2$ 98.44.

Anabasine picrate was prepared by addition of a solution of 1 g of picric acid in 70 ml of water to 0.25 g of anabasine in 10 ml of water. After recrystallization from hot water, the picrate melted at 201-202°.

α_1 -Aminoanabasine

50 g of anabasine, 31 g of sodium amide and 150 g of vaseline oil were heated on an oil bath to 150° for 9 hours until hydrogen evolution ceased; 4.9 liters of hydrogen in all were evolved. The reaction product was treated with water, acidified with hydrochloric acid, and after separation of the aqueous layer, the filtrate was decomposed with alkali. The thick mass which formed was extracted with ether, the solution was dried with potash, the ether distilled off; the residue was vacuum distilled at 8 mm. After recrystallization from toluene, 11 g of α_1 -aminoanabasine (22% in relation to the anabasine) with a m.p. of 108-109° was obtained.

0.0792 g sub.: 0.1956 g CO_2 ; 0.0572 g H_2O . 0.1524 g sub.: 0.3773 g CO_2 ; 0.1112 g H_2O . 0.0942 g sub.: 18.3 ml N_2 (10°, 766 mm). 0.0708 g sub.: 13.9 ml N_2 (12°, 766 mm). Found %: C 67.53, 67.60; H 8.10, 8.16; N 23.41, 23.48. $C_{10}H_{14}N_2$. Calculated %: C 67.79; H 8.41; N 23.72.

α_1 -Chloroanabasine

18 g of α_1 -aminoanabasine was dissolved in 30 ml of hydrochloric acid (d 1.19), the solution was saturated with hydrogen chloride, and then small portions of powdered sodium nitrite were added at 30-35° (the addition of the latter was regulated with starch-iodine paper). The solution was further heated on a water bath initially to 60° and then on a boiling water bath; after nitrogen evolution had ceased the cooled mass was treated with potassium hydroxide solution. Two layers were thereupon formed: an upper oily layer and a lower aqueous layer. After extracting the aqueous layer with ether and drying the ethereal solution with roasted potash, the ether was distilled off and the oily liquid was subjected to fractional distillation. A heavy oil distilled over at 134° (3 mm); it quickly crystallized and after recrystallization from gasoline 6.3 g of a substance with a m.p. of 99° (35% of the theoretical) was obtained.

0.1248 g sub.: 0.092 g AgCl. 0.1978 g sub.: 0.1411 g AgCl. 0.1130 g sub.: 13.10 ml N_2 (10°, 765 mm). 0.1410 g sub.: 16.5 ml N_2 (10°, 765 mm). Found %: Cl 18.23, 17.76; N 13.96, 14.11. $C_{10}H_{13}N_2Cl$. Calculated %: Cl 18.05; N 14.25.

α_1 -Chloroanabasine consisted of colorless crystals, soluble in water (1:100), alcohol and ether.

α_1 -Chloronicotinic Acid

5.5 g of α_1 -chloroanabasine in 500 ml of water was oxidized with 40 g of potassium permanganate, which was added in small portions. The decolorization proceeded very quickly. The reaction mixture was filtered off from the manganese dioxide; the filtrate, after neutralization with sulfuric acid, was concentrated to small volume, and the residue acidified with 10% sulfuric acid; crystals were thereupon formed which, after having been recrystallized from hot water, melted at 199°. 3.3 g (60%) was obtained.

0.1922 g sub.: 0.1774 g AgCl. 0.2012 g sub.: 0.1812 g AgCl. 0.1828 g sub.: 13 ml N_2 (12°, 769 mm). 0.1921 g sub.: 14.4 ml N_2 (12°, 769 mm). Found %: Cl 22.21, 22.29; N 8.54, 8.99. $C_6H_4O_2NCl$. Calculated %: Cl 22.49; N 8.89.

The α_1 -chloronicotinic acid consisted of colorless crystals, slightly soluble in cold water and quite soluble in alcohol and alkalis.

α_1 -Aminonicotinic Acid

2 g of α_1 -chloronicotinic acid was heated in a sealed tube with excess 30% ammonia solution at 170° for 8 hours; after opening the tube, the solution was concentrated until it crystallized. After filtration and washing with water and alcohol until the chlorides had been completely eliminated, the substance was recrystallized from hot water; m.p. 298-300°; the yield was 1 g, which was equivalent to 50% of the theoretical.

0.2524 g sub.: 0.4819 g CO₂; 0.0864 g H₂O. 0.3112 g sub.: 0.5924 g CO₂; 0.1201 g H₂O. Found %: C 52.09, 51.92; H 4.37, 4.31. C₆H₆O₂N₂. Calculated %: C 52.17; H 4.34.

Ethyl Ester of α_1 -Aminonicotinic Acid

3 g of α_1 -aminonicotinic acid in a mixture with 5 ml of absolute alcohol, and 3-5 ml of concentrated sulfuric acid were heated on a water bath with a reflux condenser for 9 hours. After cooling, the reaction mixture was treated with soda solution; a precipitate thereupon settled out which, after recrystallization from water, melted at 149-150°; the yield was 1.2 g (40%).

0.1032 g sub.: 0.2180 g CO₂; 0.0553 g H₂O. 0.1424 g sub.: 0.3012 g CO₂; 0.0760 g H₂O. 0.1046 g sub.: 14.3 ml N₂ (12°, 768 mm). 0.0792 g sub.: 10.8 ml N₂ (12°, 770 mm). 0.0242 g sub.: 0.5962 g camphor: Δt 12°. 0.0207 g sub.: 0.4970 g camphor: Δt 13°. Found %: C 57.62, 57.69; H 5.98, 5.97; N 16.39, 16.38. M 168.5, 159.6. C₈H₁₀O₂N₂. Calculated %: C 57.83; H 6.02; N 16.86. M 166.

The ethyl ester of α_1 -aminonicotinic acid consisted of colorless silky crystals, which were insoluble in water, alcohol and ether, and soluble in hot water and in chloroform. The ester was saponified by heating 1 g with 5-8 ml of a 20 % aqueous solution of sodium hydroxide with a reflux condenser on a oil bath to 150° for 3 hours. A precipitate was formed during neutralization with sulfuric acid which melted at 298-300°, after recrystallization from hot water, and displayed no melting point depression in a mixed sample with α_1 -aminonicotinic acid. During the addition of a solution of iodine in potassium iodide to the solution which had been rendered alkaline (after the α_1 -aminonicotinic acid had been filtered off) and subsequent heating, the mixture manifested the odor of iodoform.

On saturating a 5% chloroform solution of the ethyl ester of α_1 -aminonicotinic acid with hydrogen chloride, and after distilling off the solvent, a precipitate was formed which, after having been recrystallized from chloroform, melted at 191-192° and was quite soluble in water and alcohol.

0.3104 g sub.: 16 ml 0.095 N KOH. 0.2994 g sub.: 15.5 ml 0.095 N KOH. Found %: C₈H₁₀O₂N₂ · HCl 98.84, 99.27.

Amide of α_1 -Aminonicotinic Acid

1 g of the ethyl ester of α_1 -aminonicotinic acid was heated at 150-160° with a concentrated alcoholic solution of ammonia in a sealed tube for 6 hours. The reaction product was concentrated until it crystallized; after recrystallization from hot water, it melted at 312°. The yield was 0.42 g (42%).

0.2004 g sub.: 0.3840 g CO₂; 0.0897 g H₂O. 0.2212 g sub.: 0.4220 g CO₂. 0.0984 g H₂O. 0.0521 g sub.: 13.10 ml N₂ (10°, 764 mm). 0.0481 g sub.: 12.3 ml N₂ (10°, 766 mm). Found %: C 52.32, 52.04; H 5.00, 4.98; N 30.29, 30.86. C₆H₇ON₂. Calculated %: C 52.55; H 5.11; N 30.65.

SUMMARY

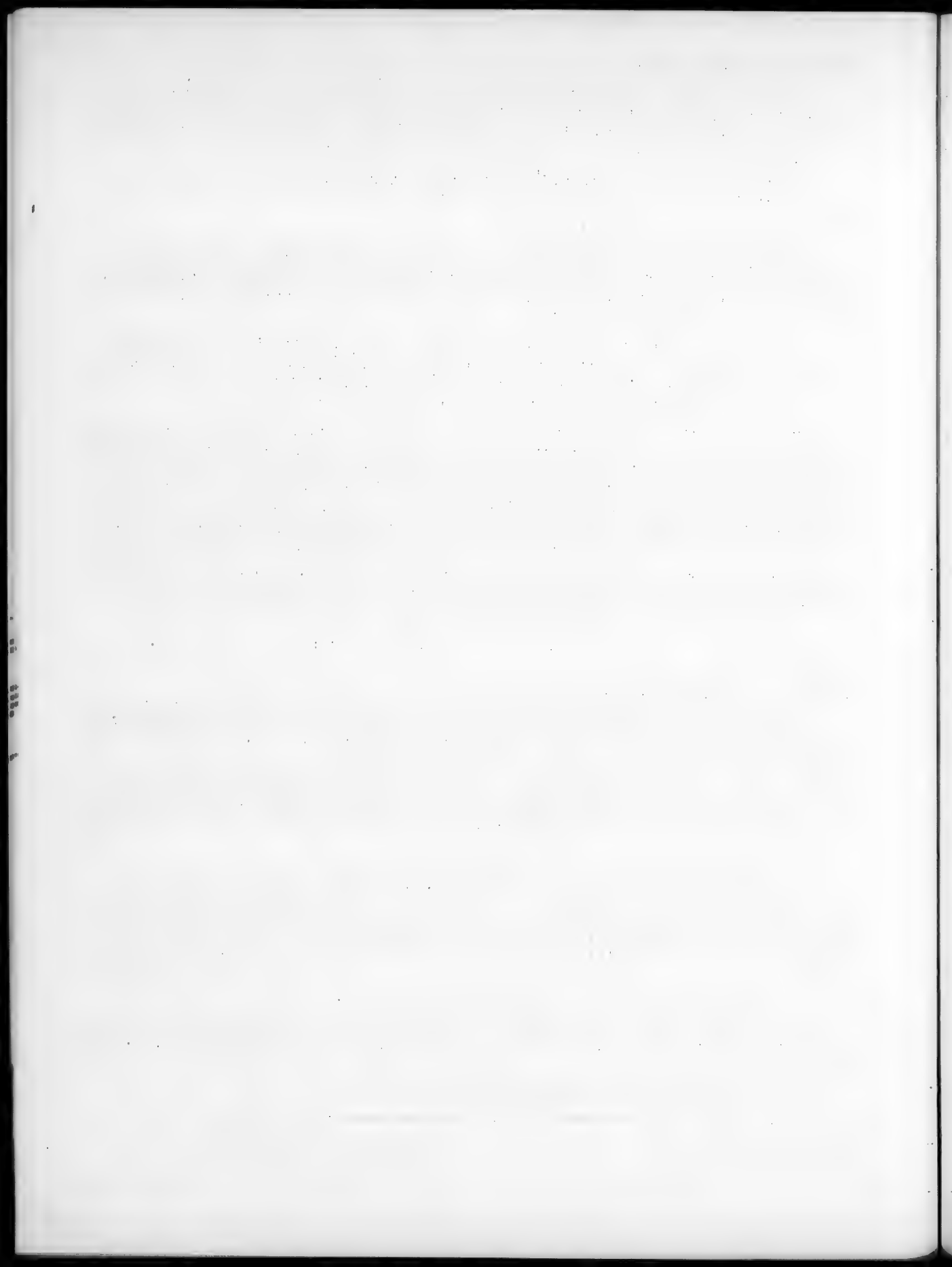
The methods of synthesizing the ethyl ester and amide of α_1 -aminonicotinic acid, starting from technical anabasine sulfate, were studied. It was found that the indicated ester can be prepared by the oxidation of α_1 -chloroanabasine with subsequent amination and esterification of the α_1 -aminonicotinic acid which is formed. The amide of α_1 -aminonicotinic acid is formed by treating the ethyl ester of α_1 -aminonicotinic acid with ammonia under pressure.

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SYNTHESIS AND PROPERTIES OF AZOMETHINES FROM WEAKLY BASIC AROMATIC AMINES

B. A. Porai-Koshits and A. L. Remizov

One of the authors of the present communication and E. M. Poznanskaya [1], in the course of studying the acid hydrolysis of azomethines, concluded that this reaction proceeds via a stage of formation of an intermediate water addition product to azomethine, which consists of an amino alcohol of the structure $R-CHOH-NH-R'$ (where R and R' are aromatic radicals).

On the other hand, Hantzsch [2] and Dimroth [3] showed in due course, that an intermediate amino alcohol of exactly the same structure is formed as a result of the addition of an amine molecule to aldehyde in the process of synthesizing azomethines. This intermediate reaction product, distinguished by a remarkable lability, depending on the conditions and the composition, is either decomposed into the initial components (i.e., amine and aldehyde), or is converted into a stable azomethine, thereby losing a molecule of water.

Since the hydrolysis of azomethines and their synthesis by the reaction of primary amines with aldehydes proceeds through a stage of formation of the same intermediate product, both these processes represent opposed directions of the same reversible reaction, which can be depicted by the scheme which follows below:



where R and R' are aromatic radicals.

It is ordinarily considered that all aromatic azomethines are completely stable in neutral medium and undergo hydrolytic cleavage into amine and aldehyde only in the presence of mineral acids. However, this is not actually the case. In the course of working with azomethines prepared from aromatic amines with weakly basic properties (nitroanilines, streptocidin) we were able to satisfy ourselves that such azomethines were far from inert to the action of moisture, even in the complete absence of acid.

We found, for example, that benzal-p-nitroaniline is decomposed into p-nitroaniline and benzaldehyde during any prolonged boiling of its solutions in suitable non-dehydrated polar solvents (the lower alcohols, acetone). For this very reason, its crystallization from similar solvents ultimately yields pure p-nitroaniline [1]. The sensitivity of benzal-p-nitroaniline to the action of moisture is so great that it does not resist prolonged storage in moist air. We had to observe the very same thing, although to an appreciably lesser extent in the work with benzylidene derivatives of m-nitroaniline and streptocidin (sulfanilamide). This property of azomethines prepared from weakly basic aromatic amines is direct evidence of the reversibility of the reaction resulting in their formation from the corresponding amines and aldehydes.

The position of the equilibrium of such a reaction is to the highest degree dependent, apparently, on the degree of basicity of the initial amine: the weaker its basic properties, the more strongly the equilibrium is displaced to the left, and the lower, consequently, the yield of azomethine.

As the voluminous experimental material available in the chemical literature concerning the synthesis of all kinds of azomethines shows, the reaction between primary aromatic amines and aromatic aldehydes proceeds with varying readiness, depending on the character of the aldehyde and amine components; the properties of the latter (degree of basicity) are predominate.

Aniline, and especially those of its derivatives which contain nucleophile substituents in the nucleus (OH, OAlk, Alk), react with aldehydes in the cold, and the reaction is accompanied by the evolution of heat, while amines which have a very low basicity (for example nitroanilines), react with appreciable difficulty. The directions set forth in the literature envisage in such cases the heating of the amine with a great (ordinarily two-fold) excess of the aldehyde at 150-180° until complete cessation of the evolution of water [4, 5] occurs. The azomethine thus obtained proved to be contaminated with excess aldehyde and the products of its oxidation and polymerization.

Taking into account that the reaction between primary aromatic amines and aromatic aldehydes proceeds reversibly, we accomplished the synthesis of azomethines from weakly basic amines in another manner, to wit, by

eliminating the water which was formed in the reaction from its vicinity as it was formed. The need to take a considerable excess of aldehyde and to carry out the process at high temperature was thereby eliminated. The reaction was carried out in boiling toluene or xylene with simultaneous elimination of a portion of the solvent by distillation, with the vapors of which the reaction water (in the form of an azeotropic mixture) was also eliminated.

Azomethines were synthesized by this method from *p*- and *m*-nitroanilines and streptocidin (sulfanilamide) with almost quantitative yields in the presence of a minimum excess of aldehyde (5-15%). The preparations obtained were initially so pure that it was often almost unnecessary to further purify them.

EXPERIMENTAL

Benzal-*p*-nitroaniline. Into a reaction beaker supplied with a stirrer (with a mercury seal) and joined with the aid of a small branched fractionating column (with a thermometer) with a straight condenser, 50 ml of toluene or xylene was poured, after which 13.8 g (0.1 mole) of powdered purified *p*-nitroaniline was inserted while the mixture was being energetically stirred. A solution of 11.7 g (0.11 mole) of benzaldehyde in 25 ml of the given solvent (toluene or xylene) was added to the uniform suspension, which was being formed while it was being continually stirred. The beaker was then covered with a cork stopper, connected with the rest of the apparatus and, while the stirrer was operating, was heated on a glycerin bath so that boiling of the solvent, which quickly began to distill, proceeded energetically, but regularly. To facilitate the distillation, the fractionating column was initially slightly heated with a smoking gas burner flame.

The first portion of the distillate contained a large quantity of reaction water and went over at a temperature of 85-100°, the temperature then began to rise gradually. After 25 ml of moist distillate had collected in a graduated cylinder, 20 ml of fresh solvent was added to the reaction beaker (through the fractionating column) and the distillation was continued. This operation was repeated several times until 25 ml of completely transparent distillate could be collected which had distilled over at the boiling temperature of the pure solvent. After this, the addition to the reaction beaker of fresh solvent was discontinued and its contents, consisting of completely homogeneous solution, were poured out into a vessel for crystallization, where it was somewhat cooled and diluted with an equal volume of ether. The very well-formed, light yellow crystals which were evolved were separated, initially washed with benzene and then with gasoline, and dried at a temperature of 70-80°.

The yield of uncrystallized product with a m.p. of 110-115° was 20-20.5 g (88-92%).

Azomethine was obtained in a higher yield (95% and higher) in toluene than in xylene, but on the other hand, the synthesis required twice as much time (3-4 hours instead of 1.5-2 hours).

The benzal-*p*-nitroaniline thus obtained, recrystallized from toluene or xylene with ether, had a m.p. of 117-118° which was equivalent to the literature data [4]. It consisted of slightly yellowish, almost colorless (but not yellow as was indicated in the literature), well-formed short prisms (under the microscope), which yellowed in air as a consequence of hydrolysis, accompanied by the formation of *p*-nitroaniline. In alcoholic and acetone solutions it quickly decomposed and, therefore, crystallization of it from these solvents, even when rendered anhydrous in the usual way, resulted in pure *p*-nitroaniline.

***m*-Nitrobenzal-*p*-nitroaniline.** This azomethine was prepared analogously to benzal-*p*-nitroaniline from *p*-nitroaniline and *m*-nitrobenzaldehyde, taken in a 5% excess in toluene with a yield of 98% of the theoretical.

After crystallization from benzene it had the m.p. of 146°, indicated for it in the literature [5].

Benzal-*m*-nitroaniline. The reaction between *m*-nitroaniline (13.8 g—0.1 mole) and benzaldehyde (11.7 g—0.11 mole) was carried out in boiling toluene. After completion of the elimination of the moist solvent, the hot toluene solution of the azomethine obtained was diluted with gasoline until crystallization began and cooled in ice water. The crystals which precipitated were drawn off, washed on a funnel with gasoline and dried in air.

The yield was 21 g (92-93%). M.p. 70-71°.

After crystallization from toluene with gasoline, the azomethine was obtained in the form of almost colorless needles with a m.p. of 71.5-72°, which slowly yellowed when kept in moist air. During crystallization from insufficiently well-dried non-polar solvents, it appreciably hydrolyzed. The mother liquor, after such crystallization, contained a large amount of *m*-nitroaniline.

Benzalstreptocidin. The preparation of benzalstreptocidin was carried out in the same apparatus and in the same manner as the above described synthesis of benzal-*p*-nitroaniline. However, as a consequence of the almost complete insolubility of streptocidin and its benzylidene derivative in non-polar solvents, the process of forming the azomethine was carried out in a heterogeneous medium and, therefore, required considerable time. 17.2 g of

streptocidin (0.1 mole) was stirred with a solution of 12.0-12.5 g (0.113-0.118 mole) of benzaldehyde in 75 ml of xylene and the suspension which was formed was heated while being energetically stirred until the solvent boiled; this was accompanied by its slow distillation. After the reaction was completed (cessation of the distillation of moist xylene), the reaction mass was cooled, the precipitate filtered off and washed on the filter successively with benzene, ether and gasoline. The yield of crude product with a m.p. 174-177° (corrected) was around 23 g (88-89%).

Benzalstreptocidin recrystallized from dioxane or a large volume of absolute alcohol with benzene consisted of shiny snow white leaflets which slowly melted with a little decomposition at 178.0-179.2° (corrected),* were soluble in alkali with partial hydrolysis, very slightly soluble in aromatic hydrocarbons and other non-polar solvents, but considerably better soluble in pyridine, hot dioxane and benzyl alcohol. The azomethine was somewhat soluble in boiling acetone and ethanol, and underwent considerable hydrolysis in these solvents. The residue after elimination of the acetone or alcohol contained chiefly streptocidin and products of the condensation and oxidation of benzaldehyde.

SUMMARY

1. It was shown by the analysis of the condensation mechanism of primary aromatic amines with aromatic aldehydes that the process of formation of aromatic azomethines is reversible.
2. It was found that azomethines formed from aromatic amines with feebly basic properties are readily hydrolyzed under the influence of moisture even in the absence of acid, which is not characteristic of azomethines formed from comparatively highly basic aromatic amines.
3. It was concluded on the basis of the preceding that the equilibrium of the reaction involving the formation of azomethine is the more displaced toward the left (i.e., in the direction of hydrolysis) the less the basic properties of the amine which participates in it. This conclusion is confirmed also by comparison of the degree of basicity of various primary aromatic amines with data known in the literature concerning their activity in the reaction with aromatic aldehydes.
4. A method of synthesizing azomethines from weakly basic primary aromatic amines was worked out which does not require the use of a large excess of aldehyde, and which ensures a high yield and quality of the reaction product.

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* A m.p. of 174° [6] is cited in the literature for benzalstreptocidin, while according to other data it is 204° [7].

SYNTHESIS AND PHYSIOLOGICAL ACTIVITY ON PLANTS OF ISOPROPYL ESTERS OF CERTAIN ARYL CARBAMIC ACIDS

Yu. A. Baskakov and N. N. Melnikov

Together with the use of chemical agents in the fight against diseases and parasites of plants, chemical agents have obtained a rather wide use in the last few years in the struggle against weeds and as stimulators of plant growth. The scale of the use of this type of substances has continuously broadened. The most well-studied substances are used for the fight against dicotyledonous weeds as stimulators of root formation and to obtain seedless fruit [1-8]. However, great interest also attaches to another group of compounds used as herbicides in the struggle against herbaceous weeds. The simplest representative of this group of compounds is the isopropyl ester of phenylcarbamic acid, which finds use in the struggle against herbaceous weeds in the young crops of dicotyledonous plants [1, 9]. The isopropyl ester of 3-chlorophenylcarbamic acid is distinguished by an even greater activity, which several times exceeds the isopropyl ester of phenylcarbamic acid in force of action, and is more stable in the ground [10, 11].

In spite of the rather wide application of the two indicated substances in agriculture, the mechanism of the action on plants of this group of compounds has hardly been studied at all. The influence of the structure of the aromatic radical on the activity of the compound has not been studied either. It is only known that of the various esters of phenylcarbamic acid the isopropyl ester is distinguished by the strongest action on grasses [12].

A very limited number of the isopropyl esters of arylcarbamic acids containing various functional groups in the aromatic radical has been described. The most important constants have not been indicated in the literature even for the widely used 3-chlorophenylisopropylcarbamate.

In connection with what has been set forth, we undertook the present work involving the synthesis and study of the physiological activity on plants of certain isopropyl esters of arylcarbamic acids.

We accomplished the synthesis of the isopropyl esters of arylcarbamic acids by the reaction of the corresponding amines with the isopropyl ester of chlorocarbonic acid in the presence of pyridine [13].











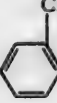
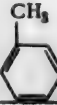
The compounds obtained by us and their properties are set forth in the table. It is of interest to note that the corresponding esters were not successfully obtained from the 2,6-dichloro-, 2,4,6-trichloro- and 2,3,5,6-tetrachloroanilines. This behavior of the enumerated amines can be explained by the presence of steric hindrance, since both positions ortho to the amino group are occupied.

The study of the physiological activity of the compounds obtained by us was carried out on wheat shoots of the Lyutescens-62 type.

100 wheat grains were treated with a determined quantity of a mixture of the substance being investigated with kaolin (carefully mixed and ground into a fine powder which passed through a No. 85 sieve), placed in a cuvette on moist filter paper and kept in a thermostat at 20-22° for 7 days. The calculation was carried out after the passage of this period. The minimum concentration of the substance which caused complete stoppage of the growth in half of the shoots was determined for all the compounds. The compounds which did not cause stoppage of the growth of the germinating grains of wheat in a concentration of 50 mg of 5% powder on kaolin per 100 grains of wheat were considered inactive. The data for the activity of the compounds studied by us are set forth in the table. The activity of the isopropyl ester of phenylcarbamic acid is set forth in the table for comparison. All the compounds synthesized by us turned out to be inactive in the tests on radish shoots.

The data obtained permit us to draw the following conclusions concerning the dependence of the physiological activity of the isopropyl esters of arylcarbamic acids on the structure of the aromatic radical.

1) Substitution for the hydrogen in the ortho- and para- positions to the amido group in the phenyl radical of the isopropyl ester of the phenylcarbamic acid by various functional groups leads to a sharp reduction in the activity of the compound. All the para- substituted phenylisopropylcarbamates were inactive; although the ortho

Structural formula	Yield (in %)	M.p. (in °)	Empirical formula	Analysis for nitrogen		Minimum concentration of the substance which caused complete inhibition of the growth in 50% of the shoots	
				found	calculated	% content in the mixture with kaolin	weight of the sample of the mixture of the substance with kaolin per 100 grains of wheat (in mg)
 NHCOOC ₃ H ₇	-	-	-	-	-	0.025	30
 NHCOOC ₃ H ₇	94	..	C ₁₀ H ₁₂ O ₂ NCl	6.54; 6.32	6.54	1	30
 NHCOOC ₃ H ₇	91	...	C ₁₀ H ₁₂ O ₂ NCl	6.58; 6.50	6.54	0.01	30
 NHCOOC ₃ H ₇	96	104	C ₁₀ H ₁₂ O ₂ NCl	6.43; 6.40	6.54	Inactive	-
 NHCOOC ₃ H ₇	76	105	C ₁₀ H ₁₂ O ₂ NBr	5.49; 5.33	5.42	Inactive	-
 NHCOOC ₃ H ₇	72	115	C ₁₀ H ₁₂ O ₂ NI	4.46; 4.43	4.60	Inactive	-
 NHCOOC ₃ H ₇	90	91	C ₁₀ H ₁₂ O ₄ N ₂	12.44; 12.20	12.50	0.5	30
 NHCOOC ₃ H ₇	93	107	C ₁₀ H ₁₂ O ₄ N ₂	12.25; 12.36	12.50	Inactive	-
 NHCOOC ₃ H ₇	91	62	C ₁₁ H ₁₅ O ₂ N	7.32; 7.31	7.25	5	30
 NHCOOC ₃ H ₇	82	90	C ₁₁ H ₁₅ O ₂ N	7.46; 7.21	7.25	0.025	20

• B.p. 84° (1 mm); d_4^{20} 1.1773; n_D^{20} 1.5304.

.. B.p. 112-113° (1 mm); d_4^{20} 1.1913; n_D^{20} 1.5402.

... B.p. 127-130° (1 mm); d_4^{20} 1.1032; n_D^{20} 1.5247.

(continued)

1	2	3	4	5	6	7	8
	95	52	$C_{11}H_{15}O_2N$	7.13; 7.21	7.25	Inactive	-
	96	----	$C_{11}H_{15}O_3N$	6.48; 6.68	6.70	5	20
	86	80	$C_{10}H_{11}O_2NCl_2$	5.82; 5.74	5.65	Inactive	-
	84	70	$C_{10}H_{11}O_2NCl_2$	5.53; 5.41	5.65	1	30
	90	40	$C_{11}H_{14}O_2NCl$	6.32; 6.17	6.15	Inactive	-
	90	113	$C_{11}H_{14}O_2NCl$	6.20; 6.31	6.15	Inactive	-
	83	27-29	$C_{11}H_{14}O_2NBr$	5.29; 5.17	5.14	Inactive	-
	88	114	$C_{10}H_{10}O_2NCl_2$	4.94; 4.92	4.96	2.5	30
	73	134	$C_{15}H_{22}O_4N_2$	9.37; 9.32	9.52	Inactive	-
	-	-	-	-	-	Stimulates growth	-
	-	-	-	-	-	Stimulates growth	-

derivatives had some physiological activity, it was, however, inferior to that of phenylisopropylcarbamate. In the series of ortho-substituted phenylisopropylcarbamates, the most active were the halogen derivatives and the least active the methyl derivatives.

It is of interest to note that parachlorophenyldimethylurea, close in structure to parachlorophenylisopropylcarbamate, has high activity and finds application as a herbicide with a selective action [14]. This indicates a different mechanism for the action on plants even of compounds which are so close in structure.

2) Substitution for the hydrogen in the meta- position to the amido group in the phenyl radical of the phenylisopropylcarbamate by substituents of the first series leads to substantial increase in the activity of the compound, while substituents of the second series lower the activity of the compound.

Such an influence of the position and character of the substituent in the aromatic radical of the esters of arylcarbamic acids on their physiological activity indicates their varying stability and behavior in plants and the different character of the reaction with enzymes. The rapid destruction of p-chloroaniline in the presence of peroxidase [15] can serve as a well-known confirmation of this.

3. The introduction of two substituents into the phenyl radical of the phenylisopropylcarbamate leads to a substantial reduction in the activity of the compound. An analogous picture is also observed in the case of the tri-substituted compounds. The reduction in the activity occurs to a lesser extent if one of the substituents of the first series is found in position 3 to the amide group.

It is of interest that diphenylethylcarbamate and ethylphenylethylcarbamate do not inhibit but stimulate the growth of wheat shoots.

EXPERIMENTAL

The preparation of the isopropyl esters of arylcarbamic acids was carried out by us under the following conditions: 0.05-0.1 mole of amine and an equimolecular quantity of pyridine were dissolved in 25-50 ml of ether and a solution of an equimolecular quantity of isopropylchlorocarbonate in 25-50 ml of ether was gradually added to the well-stirred solution obtained. The addition of isopropylchlorocarbonate was carried over the course of 10-15 minutes, after which the reaction mixture was boiled with a reflux condenser for 1 hour. After completion of the reaction, 40 ml of water was added to the reaction mixture, the aqueous layer was separated off, and the ethereal layer was washed with a 5% aqueous solution of hydrogen chloride and water. The ethereal solution was then further dried over magnesium sulfate, the ether was evaporated off and the residue was vacuum distilled or recrystallized from low boiling gasoline or petroleum ether. The compounds obtained by us and their constants are set forth in the table.

In conclusion we deem it necessary to express our gratitude to P. A. Genkel and E. Z. Okina for their valuable suggestions concerning the testing of the physiological activity of the compounds synthesized by us.

SUMMARY

A number of isopropyl esters of arylcarbamic acids which had not been described in the literature were synthesized and their activity on wheat shoots was studied. It was established that substitution for the hydrogen in the phenyl radical of the phenylisopropylcarbamate substantially influences the activity of the compound. The para- and ortho- isomers are considerably less active than the corresponding meta- isomers.

It was shown that the selective action of these compounds on monocotyledonous plants is preserved when functional groups are introduced into the phenyl radical.

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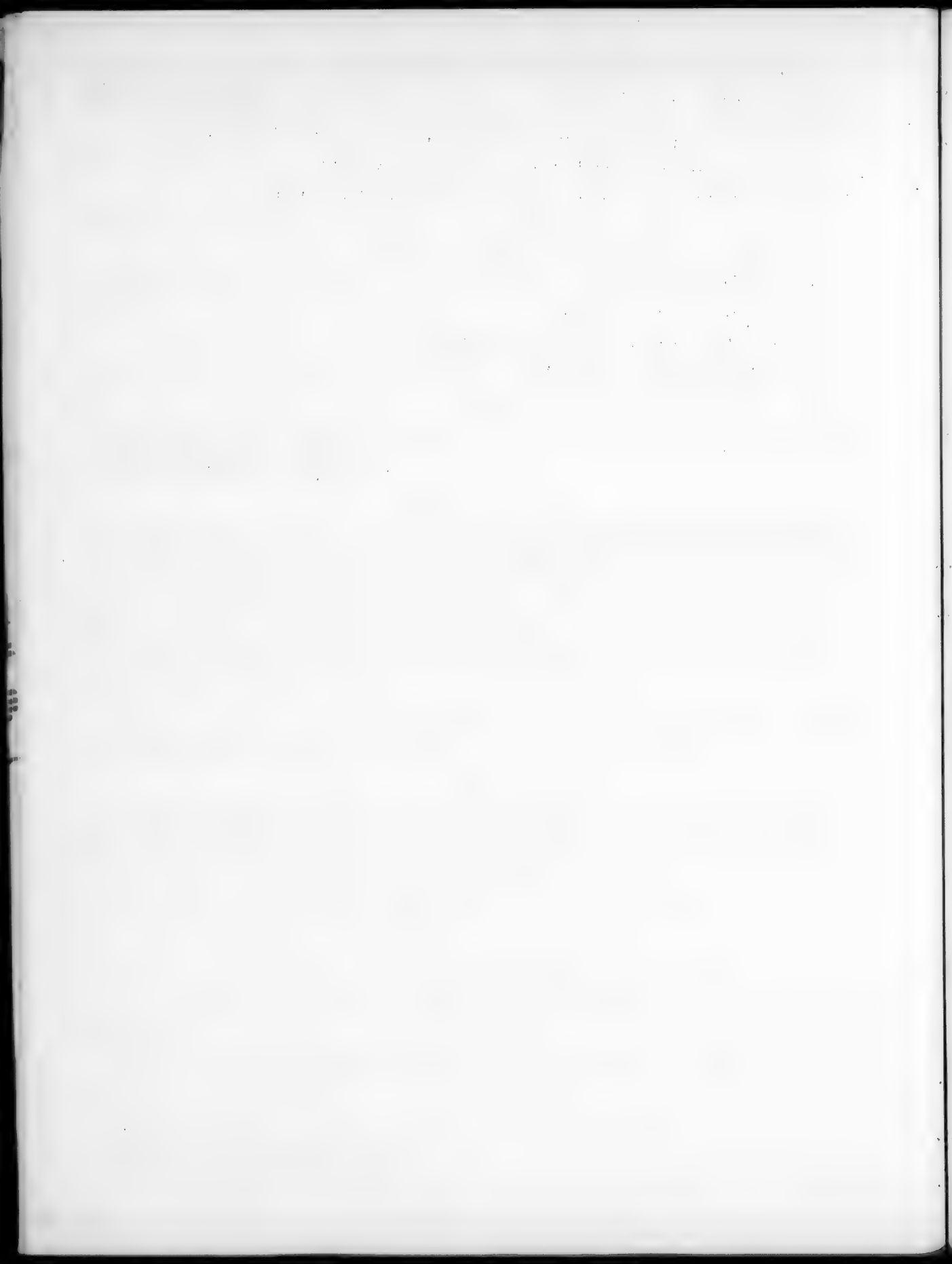
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SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS FROM HYDROCARBONS

AND THEIR DERIVATIVES

III. REACTION OF ACETYLENIC HYDROCARBONS WITH PHOSPHORUS TRICHLORIDE AND OXYGEN

Yu. M. Zinovyev, L. I. Muler and L. Z. Soborovsky

It has previously been shown [1-2], that paraffinic and ethylenic hydrocarbons react with phosphorus trichloride and oxygen with the formation of the acid chlorides of alkan- and chloroalkenophosphinic acids; the reaction with chloro substituted paraffins and chloroolefins proceeds analogously.

The reaction of a number of acetylenic hydrocarbons with phosphorus trichloride and oxygen has been studied in the present work. It was preliminarily established that, similarly to the saturated hydrocarbons and olefins, neither acetylene nor other acetylenic hydrocarbons enter into reaction with phosphorus trichloride in the absence of oxygen. Equally, the reaction does not occur with phosphorus oxychloride. In the presence of oxygen, these hydrocarbons react with phosphorus trichloride with the formation of the corresponding acid chlorides of chloroalkenophosphinic acids. The reaction can be represented by the following general scheme:

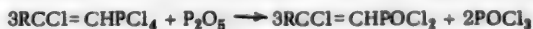


In the reaction with acetylene along with the di-acid chloride of 2-chloroethanophosphinic acid, a crystalline substance was isolated in small quantity (m.p. 60°, b.p. 135-137° at 1 mm), the analytical data of which corresponded to those of the di-acid chloride of dichloroethanodiphosphinic acid $C_2H_2Cl_2(POCl_2)_2$. The formation of this compound, in all probability, is associated with subsequent reaction of the di-acid chloride of 2-chloroethanophosphinic acid at the multiple bond with phosphorus trichloride and oxygen



The reaction of phosphorus trichloride and oxygen was achieved, aside from acetylene, with hexyne-1, vinyl- and phenylacetylenes. The yield of the corresponding di-(acid chlorides), very small for acetylene, increased with increasing molecular weight of the hydrocarbon, but nevertheless remained comparatively small (for example 24% of the theoretical in the reaction with phenylacetylene).

The structure of the di-(acid chlorides) of chloroalkenophosphinic acids obtained was established (for example of the reaction products with hexyne-1 and phenylacetylene) via comparison of the properties of their derivatives with the properties of these same compounds synthesized by another method. With this object the well-known addition reaction of phosphorus pentachloride to acetylenic hydrocarbons [3] was used. The phosphorus chloroalkenotetrachlorides prepared by this method were then converted either by treatment with phosphorus pentoxide into the acid chloride of the corresponding chloroalkenophosphinic acid [4], or by hydrolysis into the free chloroalkenophosphinic acid



The acid chlorides of chloroalkenophosphinic acids synthesized by the two methods described above were identified in the form of the aniline salts of these acids. In the determination of the melting points, a mixed sample of the aniline salts of the indicated chloroalkenophosphinic acids displayed no melting point depression.

It can, therefore, be considered as shown that the phosphorus-containing radical, entering the molecule of monosubstituted acetylenic hydrocarbons adds to the carbon atom bound with the acetylenic hydrogen, i.e., forms a compound with a structure expressed by the general formula $RCCl=CHPOCl_2$. Thus, in the reaction under consideration, as in the reaction with ethylenic hydrocarbons, the process proceeds at the point of the multiple bond. This reaction is, apparently, a consequence of the earlier considered influence on the hydrocarbon of an intermediate addition product which arises during the oxidation of phosphorus trichloride with oxygen [2].

TABLE

Compound	Formulas of the compounds synthesized	Temperature		d_4^{20}	n_D^{20}	MR _D		Molecular weight	
		m.p. (in °)	b.p. (in °) at pressure (mm)			found	calculated	found	calculated
I	$\text{ClCH}=\text{CHPOCl}_2$	—	60-61 (1) 184-186 (750)	1.5605	1.5065	34.17	33.89	188.5	179.39
II	$\text{ClCH}=\text{CHPO}(\text{OH})_2\text{C}_6\text{H}_5\text{NH}_2$	192-193	—	—	—	—	—	—	—
III	$\text{C}_2\text{H}_2\text{Cl}_2(\text{POCl}_2)_2$	60	135-137 (1)	—	—	—	—	—	—
IV	$\text{C}_6\text{H}_5\text{CCl}=\text{CHPOCl}_2$	—	96-97 (2.5)	1.3283	1.4981	51.97	52.36	231.6	235.49
V	$\text{C}_6\text{H}_5\text{CCl}=\text{CHPO}(\text{OH})_2\text{C}_6\text{H}_5\text{NH}_2$	163-164	—	—	—	—	—	—	—
VI	$\text{C}_6\text{H}_5\text{CCl}=\text{CHPOCl}_2$	58-59	121-123 (2.5)	—	—	—	—	246.4	255.48
VII	$\text{C}_6\text{H}_5\text{CCl}=\text{CHPO}(\text{OH})_2\text{C}_6\text{H}_5\text{NH}_2$	191	—	—	—	—	—	—	—
VIII	$\text{CH}_2=\text{CHCCl}=\text{CHPOCl}_2$	—	71-73 (4)	1.4686	1.5291	43.05	42.66	209.1	205.43
IX	$\text{CH}_2=\text{CHCCl}=\text{CHPO}(\text{OH})_2\text{C}_6\text{H}_5\text{NH}_2$	186	—	—	—	—	—	—	—

In the examples described in the present work, the formation of compounds in which the PCl_2 radical did not enter into the hydrocarbon at the multiple bond but as a result of the substitution of hydrogen atoms in the hydrocarbon radical was not observed. However, such processes cannot be considered excluded.

In the case of vinylacetylene containing both an ethylenic and an acetylenic bond, an organophosphorus compound is formed, the investigation of which showed that it was the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid, i.e., the reaction proceeds at the point of the triple bond



This conclusion is confirmed by the data of elementary analysis, the values of the molecular weight and molecular refraction, the capacity of the substance to add four atoms of bromine and the negative reaction with Ilosvay's reagent, which indicated the absence in the molecule of a hydrogen atom at the carbon with the triple bond. In addition, the indicated structure is in accord with the well-known addition reactions to vinylacetylene [5-8]. During the hydrolysis of the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid it is converted into the free acid, characterized in the form of its aniline salt. The formulas of the compounds synthesized and of the derivatives obtained from them are set forth in the table.

EXPERIMENTAL

The experiments carried out in the course of the study of the reaction of acetylenic hydrocarbons with phosphorus trichloride and oxygen were accomplished in a glass reaction vessel, supplied with a gas inlet tube with a porous plate, a socket for the thermometer and a reflux condenser. The oxygen entered into the reaction vessel from a cylinder through a rotameter. The liquid hydrocarbons were preliminarily stirred with phosphorus trichloride after which oxygen was passed through the reaction mass. A mixture of acetylene with oxygen from a gasometer was passed through phosphorus trichloride in the experiments with acetylene.

1. Reaction of Acetylene with Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chloroethanodiphosphinic acid (I). A mixture of acetylene with oxygen (1:1) was passed through phosphorus trichloride (435 g) at a rate of 6 liters per hour. 125 liters of the gaseous mixture was passed into the mixture. The weight of the reaction mass after the reaction was 455 g. The phosphorus oxychloride was distilled off from the reaction mixture at atmospheric pressure (temperature up to 110°). By vacuum distilling the residue, the following were isolated in insignificant quantity: a) a fraction with a b.p. of 60-61° (1 mm), d_4^{20} 1.5605, n_D^{20} 1.5065; b) a residue which congealed at room temperature.

The results of the analysis of the fraction boiling at 60-61° (1 mm):

7.71 mg sub.: 3.795 mg CO_2 ; 0.80 mg H_2O . 4.91 mg sub.: 2.370 mg CO_2 ; 0.79 mg H_2O . 0.0475 g sub.: 0.4986 g $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. 0.05026 g sub.: 0.5243 g $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. 0.1677 g sub.: 18.98 g benzene: Δt 0.248°. Found %: C 13.40, 13.17; H 1.4, 1.6; P 17.32, 17.21; M 182.5. $\text{C}_2\text{H}_2\text{OCl}_2\text{P}$. Calculated %: C 13.38; H 1.11; P 17.27; M 179.39.

Isolation of the acid chloride of dichloroethanodiphosphinic acid (III). The solid residue from several reactions was subjected to vacuum sublimation. The vapors from the flask for vacuum distillation were conducted through

a tube heated with oil in which the temperature was maintained at 100-120°. The condensate from the tube was directed into a receiving flask. The fractional distillation was carried out at 1.5-2 mm. The 132-137° fraction was isolated and crystallized in the receiving flask. The crystals were very hygroscopic and melted around 60°.

3.34 mg sub.: 0.95 mg CO₂; 0.79 mg H₂O. 5.08 mg sub.: 1.33 mg CO₂; 1.46 mg H₂O. 0.0693 g sub.: 0.7934 g (NH₄)₃PO₄ · 12MoO₃. 0.1388 g sub.: 1.5984 g (NH₄)₃PO₄ · 12MoO₃. Found %: C 7.61, 7.24; H 2.74, 3.12; P 18.94, 19.01. C₂H₂O₂Cl₆P₃. Calculated %: C 7.11; H 0.61; P 18.62.

Preparation of the aniline salt of 2-chloroethenophosphinic acid (II). 2.28 g of the acid chloride of 2-chloroethenophosphinic acid was hydrolyzed with 10 ml of water. The water and hydrogen chloride were eliminated in a vacuum.

The residue (a thick oil) was dissolved in 7 ml of ethyl alcohol, and 1.3 g of aniline in 8 ml of alcohol was added to the solution. The crystals which precipitated were separated, washed with cold alcohol and recrystallized from acetone. M.p. 192-193°.

4.70 mg sub.: 6.908 mg CO₂; 1.830 mg H₂O. 3.45 mg sub.: 5.110 mg CO₂; 1.275 mg H₂O. 0.0392 g sub.: 0.3158 g (NH₄)₃PO₄ · 12MoO₃. 0.0400 g sub.: 0.3146 g (NH₄)₃PO₄ · 12MoO₃. 2.895 g sub.: 0.1666 ml N₂ (24°, 744 mm). 4.823 mg sub.: 0.2744 ml N₂ (27°, 744 mm). Found %: C 40.07, 39.95; H 4.30, 4.13; P 13.32, 13.01; N 6.33, 6.42. C₈H₁₁O₂ClNP. Calculated %: C 40.76; H 2.97; P 13.16; N 5.94.

2. Reaction of Hexyne-1 With Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chlorohexene-1-phosphinic-1 acid (IV). Oxygen was passed at a rate of 6 liters/hour through a mixture of 20.5 g (0.25 mole) of hexyne-1 and 151 g (1.1 mole) of phosphorus trichloride at 0-10° until evolution of heat ceased. The phosphorus oxychloride was distilled off at 40-50° (in the bath) and 40 mm. 8 g of substance which boiled at 96-97° (2.5 mm); d₄²⁰ 1.3283; n_D²⁰ 1.4981 was isolated from the residue after two fold redistillation.

5.13 mg sub.: 5.985 mg CO₂; 2.03 mg H₂O. 7.69 mg sub.: 8.905 mg CO₂; 2.95 mg H₂O. 0.1137 g sub.: 9.65 ml 0.1 N AgNO₃. 0.1144 g sub.: 9.69 ml 0.1 N AgNO₃. 10.22 mg sub.: 93.974 mg (NH₄)₃PO₄ · 12MoO₃. 9.09 mg sub.: 83.842 mg (NH₄)₃PO₄ · 12MoO₃. 0.2102 g sub.: 17.6 ml 0.1 N KBrO₃. 0.1836 g sub.: 20.16 g C₆H₆; Δt 0.2°. Found %: C 31.8, 31.6; H 4.42, 4.30; Cl**30.12, 29.4; P 13.36, 13.42; bromine number 66.98; M 231.6. C₆H₁₀OCl₃P. Calculated %: C 30.57; H 4.24; Cl**30.14; P 13.16; bromine number 67.9; M 235.19.

Preparation of the aniline salt of 2-chlorohexene-1-phosphinic-1 acid (V). 4 g of the acid chloride of 2-chlorohexene-1-phosphinic-1 acid was boiled with 35 ml of water until it completely dissolved. The water was then evaporated off in a vacuum. The residue was dissolved in 5 ml of alcohol and stirred with a solution of 2.1 g of aniline in 7 ml of alcohol. The crystals which precipitated from the solution were separated, washed initially with cold alcohol, then with ether and recrystallized from acetone. M.p. 163-164°.

13.640 mg sub.: 0.883 ml 0.05 N AgNO₃. 11.940 mg sub.: 0.783 ml 0.05 N AgNO₃. 3.498 mg sub.: 0.1660 ml N₂ (24°, 746 mm). 3.500 mg sub.: 0.1617 ml N₂ (24°, 746 mm). Found %: Cl 11.50, 11.64; N 5.37, 5.21. C₁₂H₁₉O₃NCIP. Calculated %: Cl 12.1, N 4.80.

Preparation of the acid chloride of 2-chlorohexene-1-phosphinic-1 acid from phosphorus pentachloride and hexyne-1. 16.4 g (0.2 mole) of hexyne-1 was added to a suspension of 83.4 g (0.4 mole) of phosphorus pentachloride in 150 ml of benzene which was being intensively stirred. The reaction mass was stirred for 10 hours at 30-35° and left for 30 hours at room temperature. 18.5 g of phosphorus pentoxide was then added to the reaction mixture after which the stirring was continued for 5 hours at 50°. After distilling off the benzene and the phosphorus oxychloride, the residue was fractionally distilled in a vacuum. The bulk went over at 80-100° (3 mm). During a second fractional distillation, the substance boiled at 93-95° (2 mm); d₄²⁰ 1.3636; n_D²⁰ 1.5059.***

3.767 mg sub.: 4.220 mg CO₂; 1.506 mg H₂O. 4.827 mg sub.: 5.420 mg CO₂; 2.053 mg H₂O. 0.0576 g sub.: 4.94 ml 0.1 N AgNO₃. 12.08 mg sub.: 11.72 ml 0.1 N KOH. 17.24 mg sub.: 16.09 ml 0.1 N KOH. 0.1814 mg

* The hexyne-1 was prepared by the method of Henne and Greenlee [9]. The substance boiled at 70-72° (literature data 71.4°).

** Hydrolyzable chlorine (acid chloride chlorine).

*** In view of a certain discrepancy in the values for the specific gravities and indices of refraction of the samples of the acid chlorides of the chlorohexenophosphinic acids prepared, their identification was accomplished via conversion into the aniline salt. Apparently the preparation prepared according to method [3] contained a difficultly separable admixture consisting of chlorination products of hexyne-1 with phosphorus pentachloride.

sub.: 14.4 ml 0.1 N KBrO₃. Found %: C 30.61, 30.64; H 4.48, 4.76; Cl 30.49; P 13.08, 12.58. Bromine number 63.5. C₆H₁₀OCl₃P. Calculated %: C 30.57; H 4.24; Cl 30.14; P 13.16; bromine number 67.9.

Aniline salt of 2-chlorohexene-1-phosphinic-1 acid. The aniline salt was obtained from 1.4 g of the acid chloride prepared from phosphorus pentachloride and hexyne-1 under the conditions described above. The substance, after having been recrystallized from acetone, melted at 163°. The melting point of a mixed sample of aniline salts was 163-164°.

3. Reaction of Phenylacetylene With Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chloro-2-phenylethenophosphinic acid (VI). Oxygen was passed at a rate of 8 liters per hour through a mixture of 51 g (0.5 mole) of phenylacetylene and 151 g (1.1 mole) of phosphorus trichloride at 20°. 40 liters of oxygen were passed. 417.5 g of liquid was obtained. The phosphorus oxychloride and phenylacetylene which had not reacted were distilled off at 50-60° (in a bath) and 40 mm. 22.7 g (24% of the theoretical, calculating on the basis of the phenylacetylene which had reacted) of a substance which boiled at 121-123° (2.5 mm) was isolated from the residue by fractional distillation in a vacuum. The liquid changed on standing into white crystals with a m.p. of 58-59°.

6.270 mg sub.: 8.83 mg CO₂; 1.635 mg H₂O. 3.875 mg sub.: 5.33 mg CO₂; 1.040 mg H₂O. 0.1753 g sub.: 18.9 ml 0.1 N AgNO₃. 11.855 mg sub.: 99.82 mg (NH₄)₃PO₄·12MoO₃. 16.330 mg sub.: 138.09 mg (NH₄)₃PO₄·12MoO₃. 0.1488 g sub.: 11.4 ml 0.1 N KBrO₃. 0.0707 g sub.: 15.83 g C₆H₆. Δt 0.089°. Found %: C 37.9, 38.4; H 2.92, 3.03; Cl 40.69; P 12.25, 12.29; bromine number 61.4; M 246.4. C₈H₈OCl₃P. Calculated %: C 37.55; H 2.34; Cl 41.68; P 12.13; bromine number 62.5; M 255.48.

Preparation of the aniline salt of 2-chloro-2-phenylethenophosphinic acid (VII). 0.9 g of the acid chloride of 2-chloro-2-phenylethenophosphinic acid was boiled with 100 ml of water for 2 hours. The water was then evaporated off in a vacuum. Crystals with a m.p. of 160° which were readily soluble in organic solvents were isolated from the concentrated solution in the course of 24 hours. The crystals were dissolved in 8 ml of alcohol and stirred with a solution of 1.3 g of aniline in 9 ml of alcohol. The aniline salt which precipitated was filtered off, washed with alcohol and ether and dried in a vacuum. White crystals were obtained which melted at 190-191°.

5.375 mg sub.: 10.505 mg CO₂; 2.345 mg H₂O. 4.390 mg sub.: 8.540 mg CO₂; 1.790 mg H₂O. 4.135 mg sub.: 0.180 ml N₂ (28°, 744 mm). 5.500 mg sub.: 0.230 ml N₂ (28°, 744 mm). Found %: C 53.08, 53.31; H 4.56, 4.88; N 4.63, 4.54. C₈H₁₀O₃NCIP. Calculated %: C 53.93; H 4.8; N 4.40.

Preparation of 2-chloro-2-phenylethenophosphinic acid from phosphorus pentachloride and phenylacetylene (by the method of Bergman and Bondi [3]). 10.2 g (0.1 mole) of phenylacetylene was added to an intensely stirred suspension of 41.7 g (0.2 mole) of phosphorus pentachloride in 75 ml of benzene. The mixture was left for 48 hours, after which it was added to ice water in small portions. The oil which separated out was extracted with ether and after the latter had been distilled off, crystals in the form of white needles with a m.p. of 159-160° were isolated. According to Bergman and Bondi, the m.p. is 158-160°.

Preparation of the aniline salt of 2-chloro-2-phenylethenophosphinic acid. 2.1 g of 2-chloro-2-phenylethenophosphinic acid was dissolved in 5 ml of anhydrous alcohol and stirred with a solution of 1.2 g of aniline in 5 ml of alcohol. The crystals which precipitated were separated and recrystallized from alcohol; m.p. 191°.

2.955 mg sub.: 5.920 mg CO₂; 1.405 mg H₂O. 2.705 mg sub.: 5.820 mg CO₂; 1.205 mg H₂O. 5.550 mg sub.: 37.600 mg (NH₄)₃PO₄·12MoO₃. 5.800 mg sub.: 37.350 mg (NH₄)₃PO₄·12MoO₃. Found %: C 53.94, 53.68; H 5.24, 4.98; P 9.85, 9.36. C₁₄H₁₈O₃NCIP. Calculated %: C 53.93; H 4.50; P 9.95.

The melting point of a mixed sample of the aniline salts was 191°.

4. Reaction of Vinylacetylene With Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid (VIII). Oxygen was passed at -20 to -15° at a rate of 4 liters/hour through a mixture of 26 g (0.5 mole) of vinylacetylene and 137.5 g (1 mole) of phosphorus trichloride. 36 liters of oxygen were passed. After distilling off the phosphorus oxychloride 15.5 g (15.8%) of a substance which boiled at 70-75° (2.5 mm) was isolated from the residue. During a second fractional distillation, the substance went over at 71-73° (4 mm); d₄²⁰ 1.4686; n_D²⁰ 1.5291.

6.16 mg sub.: 5.265 mg CO₂; 1.325 mg H₂O. 4.56 mg sub.: 3.895 mg CO₂; 0.900 mg H₂O. 10.80 mg sub.: 4.853 ml 0.05 N AgNO₃. 19.92 mg sub.: 5.827 ml 0.05 N AgNO₃. 0.084 g sub.: 0.7000 g (NH₄)₃PO₄·12MoO₃. 0.0595 g sub.: 0.5122 g (NH₄)₃PO₄·12MoO₃. 0.2114 g sub.: 40.5 ml 0.1 N KBrO₃. 0.1621 g sub.: 18.20 g

• Hydrolyzable chlorine (acid chloride chlorine).

C_4H_5 ; Δt : 0.218°. Found %: C 23.31, 23.29; H 2.4, 2.2; Cl 51.42, 51.82; P 13.78, 14.23; bromine number 153.4; M 209.1. $C_4H_4OCl_3P$. Calculated %: C 23.2; H 1.94; Cl 51.82; P 15.08; bromine number 155.6; M 205.43.

Preparation of the aniline salt of 2-chlorobutadiene-1,3-phosphinic-1 acid (IX). 1.6 g of the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid was heated to boiling with 25 ml of water. The water was eliminated in a vacuum. The residue was diluted with 5 ml of ethyl alcohol and stirred with a solution of 0.72 g of aniline in 5 ml of alcohol. The crystals which precipitated consisted after recrystallization from acetone of white flakes with a m.p. of 186°.

4.180 mg sub.: 6.91 mg CO_2 ; 2.270 mg H_2O . 2.835 mg sub.: 4.66 mg CO_2 ; 1.435 mg H_2O . 3.018 mg sub.: 0.1666 ml N_2 (25°, 738 mm). 4.103 mg sub.: 0.2254 ml N_2 (25°, 738 mm). Found %: C 45.08, 44.83; H 6.08, 5.66; N 6.14, 6.11. $C_{10}H_{13}O_3NClP$. Calculated %: C 45.88, H 4.97; N 5.35.

SUMMARY

The reaction involving the formation of organophosphorus compounds by the reaction of hydrocarbons or their derivatives with phosphorus trichloride and oxygen which had been previously described for paraffinic and ethylenic hydrocarbons and their chlorosubstituted derivatives, was extended to acetylenic hydrocarbons. The reaction was accomplished with acetylene, hexyne-1, phenylacetylene and vinylacetylene. The corresponding acid chlorides of chloroalkenylphosphinic acids with the general formula $R-CCl=CHPOCl_2$ were isolated and characterized.

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INVESTIGATIONS IN THE 1,2-NAPHTHO-(3',4')-FURAZAN SERIES

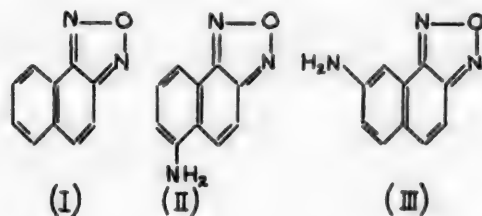
II. NITRATION AND CHLORINATION OF 1,2-NAPHTHO-(3',4')-FURAZAN

S. V. Bogdanov and S. F. Petrov

According to the data of Green and Rowe [1], the nitration of 1,2-naphtho-(3',4')-furan (I) by cooling with a 40% excess of nitric acid yields only one mononitro compound with a m.p. of 143°. This substance is stable to alkali, but is oxidized by chromic acid to 3-nitrophthalic acid. The authors assumed that the nitration product was 5- or 8-nitronaphthofurazan. With an increased excess of nitric acid, a mixture of the dinitrocompound with a small quantity of mononitro compound with a m.p. of 147° is formed. Both the dinitrocompound and the mononitrocompound are decomposed by boiling dilute alkali. A 3- or 4-nitronaphthofurazan structure is indicated for the mononitro compound, while for the dinitrocompound a 4 (or 3), 5 (or 8)- dinitronaphthofurazan structure is indicated. Nothing has been communicated concerning attempts to determine the structure of the nitrocompounds.

We obtained the nitrocompound under the conditions recommended by Green and Rowe for the nitration of naphthofurazan to 5- or 8-nitronaphthofurazan in yields exceeding that theoretically possible. It was, evidently, a mixture of the mononitro and dinitro compounds. The nitration product, prepared with the theoretical quantity of nitric acid, did not have a sharp melting point after washing with alkali and crystallization. It proved possible to convert it into an amino compound without disturbing the furazan ring. The reaction proceeded smoothly by reducing with iron in the presence of hydrochloric acid or of stannous chloride and was somewhat complicated by side reactions when sodium sulfite was used.

The reduction product proved to be a mixture of amino compounds, from which were isolated 5-amino-naphthofurazan (II) and 7-aminonaphthofurazan (III). The quantity of pure 7-aminonaphthofurazan isolated amounted to 39.6% and of the 5-isomer 26.6% of the total amino compounds. Both amino compounds were yellow colored and their salts were colorless and readily decomposed with water.



The structure of 7-aminonaphthofurazan was established by converting it (via the diazocompound) into hydroxynaphthofurazan and comparison of the latter with the 7-hydroxynaphthofurazan, obtained from 1-nitroso-2,7-dihydroxynaphthalene [2].

To demonstrate the structure of 5-aminonaphthofurazan the amino compound was converted via the diazocompound into a sulfonic acid; the latter was compared with naphthofurazan-5-sulfonic acid obtained from 2-naphthylamine-5-sulfonic acid via 2-naphthol-5-sulfonic acid and 1-nitroso-2-naphthol-5-sulfonic acid.

Consequently, the nitration of naphthofurazan during cooling, contrary to the assertion of Green and Rowe, leads to at least two compounds - 5-nitro- and 7-nitronaphthofurazan.

The 7-chloronaphthofurazan was prepared from 7-aminonaphthofurazan, while the 5-chloro- and 5-hydroxynaphthofurazans were prepared from 5-aminonaphthofurazan.

The monochloro derivative was formed by the chlorination of fused naphthofurazan in the presence of iron. This same substance was prepared by the action of potassium chlorate on a hydrochloric acid solution of naphthofurazan-3-sulfonic acid. Consequently, the direct chlorination of naphthofurazan yields 3-chloronaphthofurazan.

It can be noted that the sulfonation of naphthofurazan at 20° also led to substitution in the 3-position [3].

On treatment with potassium chlorate naphthofurazan-4-sulfonic acid in hydrochloric acid solution similarly to 3-sulfonic acid, exchanges the sulfonic group for chlorine and is converted into 4-chloronaphthofurazan.

EXPERIMENTAL

Naphthofurazan was prepared by the action of sodium hydroxide on the bisulfite compound of 1,2-naphthoquinonediaxime [4] or by the oxidation of 1-nitroso-2-naphthylamine. The latter was prepared by treating 1-nitroso-2-naphthol with ammonia [5].

The reaction was carried out in an open flask by passing gaseous ammonia through a solution of nitrosonaphthol in aqueous ammonia which was heated to 90-94°. The yield of material, cleaned by reprecipitation from hydrochloric acid, was 75% of the theoretical. Oxidation of the nitrosonaphthylamine was carried out by pouring a 5% solution of sodium hypochlorite (20% excess) into a suspension of nitrosonaphthylamine in a 10 fold quantity of 10% sodium hydroxide solution which was cooled to 0-5°; the yield of naphthofurazan, purified by steam distillation (m.p. 79°) was 88% of the theoretical. Similar results were obtained by substituting potassium ferricyanide for the hypochlorite.

Nitration of naphthofurazan. In the Green and Rowe preparation of the mononitro compound a mixture of 3.6 ml of 95% nitric acid and 15 ml of concentrated sulfuric acid was added to a cooled solution of 10 g of naphthofurazan in 100 ml of concentrated sulfuric acid. In our experiments the nitrating mixture was introduced at -2 to 0° for 40-75 minutes, the mass was stirred at 0° for 4 hours more and diluted with ice to a sulfuric acid concentration of 30-32%. The white precipitate of the nitro compound which settled out was filtered and washed with water, dilute soda solution, and again with water.

15.7 g of the nitro compound (theoretical yield of mononitro compound 12.6 g) was obtained from 10 g of naphthofurazan. Subsequently, the theoretical quantity of a 2% excess of nitric acid was used; traces of unchanged naphthofurazan remained. The water-washed nitration product, 68 g of naphthofurazan, was stirred for 30 minutes at 90-95° with 750 ml of a 7.5% solution of sodium hydroxide, filtered and subjected to analogous treatment once more. The alkali was colored during the first treatment a dark brown color, and during the second - a pale yellow color. The yield was 79.9-81.6 g, i.e., 93-95% of the theoretical. The substance had a light brown color, melted in the 132-155° range, was readily soluble in dichloroethane, acetic acid and benzene; crystallized from alcohol in the form of colorless needles with a m.p. of 138-144°.

Reduction of the nitronaphthofurazan. a) A mixture of 3 g of nitronaphthofurazan, 20.7 g of 76% stannous chloride, 39 ml of 31.5% hydrochloric acid, 80 ml of alcohol and 80 ml of water was boiled for 3 hours. After adding hot water, the tin was precipitated with hydrogen sulfide. During the addition of ammonia to the filtrate, yellow flakes of amino compound were isolated; yield: 2.15 g (83.2%).

b) A mixture of 21.5 g (0.1 mole) of nitrocompound, 500 ml of alcohol, 86 ml of water, 20 g of iron shavings and 1.5 ml of 32.5% hydrochloric acid was boiled for 6 hours. After precipitating the iron with soda, the sludge was filtered off and washed with hot alcohol. After the bulk of the alcohol had been distilled off from the filtrate, the filtrate was diluted with water and the amino compound was filtered off. The yield was 15.83 g (85.6%).

c) 372 ml of sodium sulfide solution containing 62.1 g of sodium sulfide was poured into a boiling suspension of 81.5 g of the nitrocompound in 1400 ml of alcohol, in one batch, and the mixture was boiled for 3.5 hours. After distilling off the alcohol the precipitate was filtered; the weight of the precipitate was 66.8 g. It contained 14% of admixture which was not soluble in hydrochloric acid, alkalis or in the usual organic solvents. This admixture dissolved in sulfuric acid with a red coloration and was re-isolated with water in the form of fine, bent yellow needles; it melted in the 190-220° range; contained nitrogen and did not contain sulfur. By increasing the duration of the reduction to 16 hours, the quantity of admixture was not changed, while by substituting sodium disulfide for the sulfide, it was somewhat diminished.

The amino compound obtained in these experiments melted at 132-160°, and did not yield a substance with a sharp melting point on recrystallization.

Separation of the amino compounds. 17.52 g of the amino compound obtained by the reduction of 21.5 g of the nitrocompound with sodium disulfide was boiled with 2100 ml of 4% hydrochloric acid, the insoluble residue was filtered and washed with hot 4% hydrochloric acid and with water. The weight of the residue was 1.55 g, i.e., 8.8% of the quantity of mixture taken. The hydrochloride of the amino compound precipitated when the filtrate was cooled to 40-45°. The amino compound which was isolated from this salt melted at 156-160°. After twofold

crystallization of the hydrochloride from hydrochloric acid, 7-aminonaphthofurazan with a m.p. of 161.2-161.5° was isolated. It was readily soluble in benzene and dichloroethane, crystallized from alcohol in the form of yellowish needles with a green fluorescence. The hydrochloride consisted of colorless leaflets.

4.132 mg sub.: 0.837 ml N₂ (21°, 738 mm). Found %: N 22.84. C₁₀H₇ON₂. Calculated %: N 22.70.

A yellow precipitate with a m.p. of 141-178° was isolated from the filtrate from the hydrochloride by addition of ammonia. After threefold crystallization of it from alcohol, yellow needles of 5-aminonaphthofurazan with a m.p. of 208.3-208.7° were isolated, which were readily soluble in benzene and dichloroethane. The hydrochloride consisted of short colorless prisms.

3.880 mg sub.: 0.819 ml N₂ (27°, 715 mm). Found %: N 22.57. C₁₀H₇ON₂. Calculated %: N 22.70.

The mixture of amino compounds isolated from the alcoholic filtrate after purification of the 5-amino compound, was again separated with hydrochloric acid. A total of 6.32 g (36.1% of the initial mixture) of 7-amino compound and 4.25 g (24.3% of the initial mixture) of 5-amino compound was isolated; 1.35 g of the mixture remained unseparated.

7-Chloronaphthofurazan. A solution of 2.08 g of sodium nitrite and 25 ml of sulfuric acid was poured into a solution of 4.62 g (0.025 mole) of 7-aminonaphthofurazan in 25 ml of concentrated sulfuric acid at -1°. The solution was stirred for 3 hours and diluted with ice to a concentration of 50% sulfuric acid. After eliminating the excess nitrogen oxides with urea, the diazo compound was poured into a solution of cuprous chloride in a mixture of 120 ml of 36.3% hydrochloric acid and 40 ml of water which was heated to 70-80°. The orange precipitate which settled out was a compound of chloronaphthofurazan with copper salt, to eliminate which it was twice boiled for 1 hour with 250 ml of 10% hydrochloric acid; the yield was 4.82 g. It consisted of colorless needles (from aqueous alcohol), m.p. 132.7-133.2°. It was quite soluble in organic solvents.

3.368 mg sub.: 0.415 ml N₂ (24°, 732 mm). 26.534 mg sub.: 6.491 ml 0.02 N AgNO₃. Found %: N 13.62; Cl 17.35. C₁₀H₅ON₂Cl. Calculated %: N 13.70; Cl 17.33.

7-Hydroxynaphthofurazan. The diluted solution of the diazo compound obtained as above from 4.62 g of 7-aminonaphthofurazan, was poured into 150 ml of boiling 50% sulfuric acid. The mixture was cooled, the precipitate filtered and reprecipitated from dilute sodium hydroxide; the yield was 4.23 g. It consisted of almost colorless needles (from aqueous alcohol), m.p. 217.5-218°. It was quite soluble in alcohol and benzene; alkaline solutions of it had an orange color.

3.680 mg sub.: 0.498 ml N₂ (22°, 725 mm). Found %: N 14.94. C₁₀H₆O₂N₂. Calculated %: N 15.05.

Methoxy compound. It was obtained by heating an alkaline solution of the hydroxy compound with dimethyl sulfate. It consisted of colorless needles (from aqueous alcohol), m.p. 129.8-130.2°. It was quite soluble in alcohol and benzene.

Acetoxy derivative. It was obtained by heating the hydroxy compound with acetic anhydride. It consisted of colorless needles (from aqueous alcohol), m.p. 137.0-137.4°. It was quite soluble in alcohol, benzene and acetic acid.

The 7-hydroxynaphthofurazan used for comparison was obtained by the exchange method of Nietzki and Knapp [2]. 4.73 g (0.025 mole) of 1-nitroso-2,7-dihydroxynaphthalene was dissolved in 6.32 g of 95% sodium hydroxide in 50 ml of water; 3.48 g of hydroxylamine hydrochloride was added and the liquid was boiled for 1 hour. 13 ml of 38% sodium hydroxide was added to the solution and the boiling was continued for 1 hour more. The cooled solution was diluted with 30 ml of water and the hydroxy compound was precipitated with hydrochloric acid. The yield was 3.04 g. It consisted of almost colorless needles (from aqueous alcohol), m.p. 218-218.3°. The mixture of the substance with hydroxynaphthofurazan obtained from the amino compound, melted at 218-218.3°. The acetoxy derivative consisted of needles (from aqueous alcohol), m.p. 136.7-137°; a mixture of the acetoxy derivatives melted at 137-137.3°.

5-Chloronaphthofurazan. It was prepared analogously to 7-chloronaphthofurazan from 4.62 g of 5-aminonaphthofurazan. In the given case, the chloroderivative at once precipitated in the free state and did not require treatment with hydrochloric acid. The yield was 4.75 g. It consisted of colorless needles (from aqueous alcohol), m.p. 120.2-120.8°. It was quite soluble in organic solvents.

3.380 mg sub.: 0.428 ml N₂ (27°, 728 mm). 24.041 mg sub.: 5.88 ml 0.02 N AgNO₃. Found %: N 13.80; Cl 17.34. C₁₀H₅ON₂Cl. Calculated %: N 13.70; Cl 17.33.

5-Hydroxynaphthofurazan. It was prepared analogously to the 7-hydroxy compound by the decomposition of the diazo compound from 4.62 g of 5-aminonaphthofurazan; the yield was 4.07 g. It consisted of yellow needles (from aqueous alcohol), m.p. 220.6-221.1°. It was quite soluble in organic solvents; alkaline solutions of it had an orange color.

3.247 mg sub.: 0.444 ml N₂ (25°, 733 mm). Found %: N 15.11. C₁₀H₆O₂N₂. Calculated %: N 15.05.

Methoxy derivative. It consisted of slightly yellowish needles (from alcohol), m.p. 159.1-159.5°.

Naphthofurazan-5-sulfonic acid. A solution of 2.16 g of sodium nitrite in 25 ml of sulfuric acid was poured into a solution of 4.62 g of 5-aminonaphthofurazan in 35 ml of concentrated sulfuric acid cooled to 3-4°. After stirring for 4 hours, the mixture was diluted with 270 g of ice and the excess nitrogen oxides was eliminated with urea. The solution of diazo compound was poured at 0-3° over a period of 5 minutes into a mixture of 38 ml of concentrated sulfuric acid, 400 ml of water and 46.5 g of 80.6% freshly prepared by Gattermann's method [6], copper paste which had been saturated with sulfur dioxide. A stream of sulfur dioxide was maintained while the diazo compound was being added. After stirring for an hour, the copper precipitate and the sulfonic acid were filtered off and heated to 95° with soda solution. 7 ml of 30% hydrogen peroxide was added to the filtered solution and after stirring for 2 hours the residue of hydrogen peroxide was decomposed with manganese dioxide. The solution was concentrated and the sodium salt of the sulfonic acid which precipitated was filtered; the yield was 5.3 g. It consisted of colorless needles, quite soluble in hot and poorly soluble in cold water.

0.3371 g sub.: loss on drying (150°) 0.0472 g. 0.3156 g sub.: 0.0714 g Na₂SO₄. Found %: H₂O 14.00; Na 7.32. C₁₀H₅O₄N₂Na · 2.5H₂O. Calculated %: H₂O 14.19; Na 7.25.

Sulfochloride. It was obtained by heating a mixture of the sodium salt of the sulfonic acid with phosphorus pentachloride on the water bath. It was poorly soluble in benzene. It consisted of colorless needles or elongated rhombs (from dichloroethane), m.p. 116.5-117.2°.

Amide. It consisted of prisms (from alcohol), m.p. 235.8-236.2°.

3.110 mg sub.: 0.469 ml N₂ (23°, 735 mm). Found %: N 16.81. C₁₀H₇O₃N₃S. Calculated %: N 16.86.

Synthesis of Naphthofurazan-5-sulfonic Acid From 2-Naphthol-5-sulfonic Acid

2-Naphthol-5-sulfonic acid. The pressed-out paste of the diazo compound obtained from 97.8 g (0.4 mole) of 91.3% 2-naphthylamine-5-sulfonic acid, was introduced over a period of 35 minutes into 500 ml of boiling 20% sulfuric acid. The dark red solution was neutralized with barium hydroxide and a solution of soda was poured into the solution obtained, after separating out the barium sulfate, to convert the barium salt of the sulfonic acid into the sodium salt. By partial concentration of the filtrate, 87 g 6% sodium salt of the sulfonic acid was isolated from the barium carbonate. It was quite soluble in water and crystallized in the form of long, colorless hexagonal flakes.

0.5130 g sub.: loss on drying (140°) 0.1148 g. 0.3347 g sub.: 0.0738 g Na₂SO₄. Found %: H₂O 22.38; Na 7.15. C₁₀H₇O₄SNa · 4H₂O. Calculated %: H₂O 22.63; Na 7.23.

1-Nitroso-2-naphthol-5-sulfonic acid. It was prepared analogously to 1-nitroso-2-naphthol-7-sulfonic acid [7]. The sodium salt was quite soluble in hot water and crystallized in the form of yellow needles.

0.4960 g sub.: loss on drying (120°) 0.1034 g. 0.3061 g sub.: 0.0621 g Na₂SO₄. Found %: H₂O 20.84; Na 6.57. C₁₀H₆O₅NSNa · 4H₂O. Calculated %: H₂O 20.73; Na 6.63.

Naphthofurazan-5-sulfonic acid. A mixture of 27 ml of 48.8% sodium hydroxide and 73 ml of water and then 14 g of hydroxylamine hydrochloride was added to a suspension of 34.7 g (0.1 mole) of the sodium salt of the nitroso compound in 100 ml of water. The solution was kept at 20° for 1 hour and boiled for 20 minutes. The sodium salt of the sulfonic acid which precipitated on cooling was filtered; yield 28.9 g. It consisted of colorless needles (from water).

0.2665 g sub.: loss on drying (150°) 0.0372 g. 0.2596 g sub.: 0.0581 g Na₂SO₄. Found %: H₂O 13.96; Na 7.25. C₁₀H₅O₄N₂Na · 2.5H₂O. Calculated %: H₂O 14.16; Na 7.25.

Sulfochloride. It consisted of colorless needles (from toluene), m.p. 118-118.3°. A mixture with the sulfochloride obtained via the 5-amino compound, melted at 117.2-117.8°.

Amide. It consisted of prisms (from alcohol), m.p. 236-236.3°. A mixture of the substance with the amide obtained via the 5-amino compound, melted at 236.0-236.3°.

3-Chloronaphthofurazan. a) Chlorine was passed into a mixture of 13.6 g (0.08 mole) of naphthofurazan and 0.14 g of iron powder at 78-80°. After an hour, the formation of crystals of the chloroderivative began and the mass solidified. The reaction product was introduced into a dilute soda solution, the mixture was heated to boiling, cooled, the precipitate filtered off and washed with water. The weight of the precipitate was 16.3 g, m.p. 113-131°. The precipitate was dissolved in 150 ml of hot acetic acid, 9.05 g of chloronaphthofurazan was isolated while the solution was cooled, 3.05 g more was isolated by diluting the filtrate with water; the total yield was 12.1 g, m.p. 138-142°. 1.36 g of unchanged naphthofurazan with a m.p. of 75-78.5° was isolated during further dilution of the filtrate.

It consisted of colorless needles (from alcohol or acetic acid), m.p. 144.2-144.8°. It was quite soluble in alcohol and less so in acetic acid.

44.252 mg sub.: 10.91 ml 0.2 N AgNO₃. Found %: Cl 17.48. C₁₀H₅ON₂Cl. Calculated %: Cl 17.33.

b) A solution of 1.47 g of potassium chlorate in 20 ml of water was added to a boiling solution of 2.99 g (0.01 mole) of the sodium salt of naphthofurazan-3-sulfonic acid in 160 ml of water and 5.6 ml of 35% hydrochloric acid, in the course of 3 hours. Several minutes after the beginning of the addition, white needles of chloronaphthofurazan began to precipitate. The mixture was boiled for 1 hour more, cooled, and the precipitate was filtered. The yield was 1.77 g (86.5%). M.p. 144-145.5°. It consisted of colorless needles (from alcohol), m.p. 144.8-145.5°. The melting point of the mixture of chloronaphthofurazans was 144.6-145.5°.

3.248 mg sub.: 0.399 ml N₂ (21°, 732 mm). 39.021 mg sub.: 9.54 ml 0.02 N AgNO₃. Found %: N 13.71; Cl 17.34. C₁₀H₅ON₂Cl. Calculated %: N 13.69; Cl 17.33.

4-Chloronaphthofurazan. It was prepared analogously to the 3-chloro derivative from 2.72 g (0.0094 mole) of the sodium salt of naphthofurazan-4-sulfonic acid, isolated in the fused state; yield 1.76 g (91.7%), m.p. 92-94°.

It consisted of colorless needles (from alcohol), m.p. 96.8-97.1°; quite soluble in alcohol and acetic acid.

2.942 mg sub.: 0.377 ml N₂ (28°, 719 mm). 35.458 mg sub.: 8.777 ml 0.02 N AgNO₃. Found %: N 13.72; Cl 17.55. C₁₀H₅ON₂Cl. Calculated %: N 13.69; Cl 17.33.

SUMMARY

1. Contrary to the data of Green and Rowe, by nitrating 1,2-naphtho-(3',4')-furazan in sulfuric acid in the cold with a 40% excess of nitric acid, not only the mononitro derivative, but also the dinitro derivative was obtained.
2. During the mononitration of 1,2-naphtho-(3',4')-furazan, there is formed not one nitrocompound with the nitro group in position 5- or position 8-, as Green and Rowe asserted, but two compounds: 5-nitro- and 7-nitro-1,2-naphtho-(3',4')-furazan.
3. The direct chlorination of 1,2-naphtho-(3',4')-furazan in the presence of iron leads to 3-chloro-1,2-naphtho-(3',4')-furazan.
4. The corresponding 3-chloro- and 4-chloro-1,2-naphtho-(3',4')-furazans are formed by the action of potassium chlorate on 1,2-naphtho-(3',4')-furazan-3- and 4-sulfonic acid in a hydrochloric acid medium.
5. 1,2-Naphtho-(3',4')-furazan-5-sulfonic acid is formed by the action of hydroxylamine on 1-nitroso-2-naphthol-5-sulfonic acid in alkaline medium.
6. Nitronaphthofurazans are converted by reduction into aminonaphthofurazans.
7. 5-Chloro-, 5-hydroxy-1,2-naphtho-(3',4')-furazans and 1,2-naphtho-(3',4')-furazan-5-sulfonic acid are obtained via the diazo compound from 5-amino-1,2-naphtho-(3',4')-furazan, while 7-chloro- and 7-hydroxy-1,2-naphtho-(3',4')-furazans are obtained from 7-amino-1,2-naphtho-(3',4')-furazan.

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* See Consultants Bureau Translation, page 2127.

